

Palladium-catalyzed insertion of α , β -unsaturated *N*-tosylhydrazones and trapping with carbon nucleophiles

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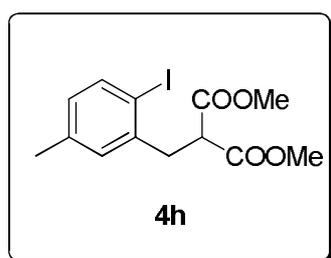
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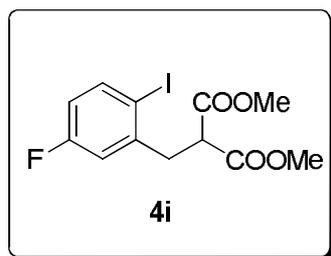
1. General Remarks

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 . All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^{13}C NMR spectra were provided. THF, and toluene, 1,4-dioxane were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN was distilled over P_2O_5 . Commercially available reagents and solvents were used without further purification. Compounds **1**¹, α , β -unsaturated *N*-tosylhydrazones **2**² and **4a**³ were synthesized according to the literature procedure.

2. Characterization Data of 4h and 4i



dimethyl 2-(2-iodo-4-methylbenzyl)malonate 4h: white solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.67 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 2.0$ Hz, 1H), 6.74 (dd, $J = 2.0$ Hz, $J = 8.4$ Hz, 1H), 3.86-3.82 (m, 1H), 3.70 (s, 6H), 3.29 (d, $J = 8.0$ Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 168.9, 139.8, 139.4, 138.3, 131.3, 129.7, 96.2, 39.2, 20.8.



dimethyl 2-(4-fluoro-2-iodobenzyl)malonate 4i: white solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.76 (dd, $J = 5.6$ Hz, $J = 8.8$ Hz, 1H), 6.99 (dd, $J = 2.8$ Hz, $J = 9.6$ Hz, 1H), 6.73-6.68 (m, 1H), 3.84-3.81 (m, 1H), 3.73 (s, 6H), 3.31 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 116.6, 164.1, 161.6, 142.4, 142.3, 140.8, 140.7, 117.8, 117.6, 116.3, 116.1, 93.1, 93.0, 52.7, 51.3, 39.3.

3. General procedure for the preparation of 3, 5 and 6

1) General procedure for the preparation of 3

Under a nitrogen atmosphere, to an oven-dried Schlenk tube were added dimethyl 2-(2-iodophenyl)malonate **1a** (0.30 mmol, 1.0 eq), *N*-tosylhydrazones **2** (0.675 mmol, 2.25 eq), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (2.5 mol%), L_2 (15 mol%), K_2CO_3 (1.575

mmol, 5.25 eq) and THF (4 mL). The mixture was stirred at room temperature for 15 minutes and then stirred at 60°C for 8h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure **3**.

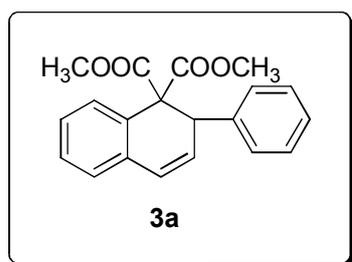
2) General procedure for the preparation of **5**

Under a nitrogen atmosphere, to an oven-dried Schlenk tube were added **4** (0.30 mmol, 1.0 eq), *N*-tosylhydrazones **2** (0.675 mmol, 2.25 eq), Pd₂(dba)₃·CHCl₃ (5 mol%), PPh₃ (30 mol%), K₂CO₃ (1.575 mmol, 5.25 eq) and THF (4 mL). The mixture was stirred at room temperature for 15 minutes and then stirred at 60°C for 5h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure **5**.

3) General procedure for the preparation of **6**

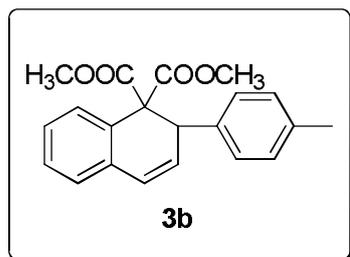
Under a nitrogen atmosphere, to an oven-dried Schlenk tube were added substituted iodobenzene (0.30 mmol, 1.0 eq), *N*-tosylhydrazones **2** (0.675 mmol, 2.25 eq), BTAC (0.6 mmol, 2.0 eq), Pd₂(dba)₃·CHCl₃ (2.5 mol%), L₃ (20 mol%), K₂CO₃ (0.9 mmol, 3.0 eq), THF (1 mL). The mixture was stirred at room temperature for 15 minutes. Meanwhile, a solution of dimethyl malonate (1.818 mmol, 6.06 eq) in THF (1 mL) was slowly added to a suspension of NaH (1.8 mmol, 6.0 eq) in THF (3 mL) at 0 °C. The remaining solution was washed with 0.5 ml of THF. The mixture was stirred at room temperature for 5 min and set aside for use in the following step. Finally, the sodium malonate solution was added to Schlenk tube via syringe and was washed with 0.5 ml of THF. Then, the reaction mixture was heated at reflux for 8h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure **6**.

4. Characterization Data of **3a-3k**

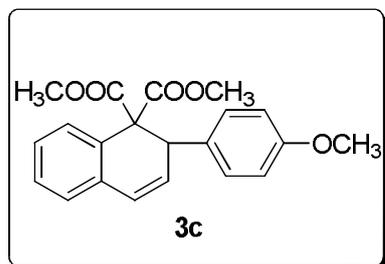


dimethyl 2-phenylnaphthalene-1,1(2H)-dicarboxylate 3a: oil. ¹H NMR (400 MHz, CDCl₃) δppm 7.56-7.54 (m, 1H), 7.30-7.22 (m, 2H), 7.19-7.09 (m, 4H), 7.07-7.04 (m, 2H), 6.51 (d, *J* = 9.6 Hz, 1H), 6.12 (dd, *J* = 6.0 Hz, *J* = 10.0 Hz, 1H), 4.51 (d, *J* = 6.0 Hz, 1H), 3.63 (s, 3H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δppm 170.1, 169.3, 137.4, 133.0, 131.7, 129.8, 128.9, 128.9, 128.4, 128.4, 128.3, 128.2, 127.7, 126.5,

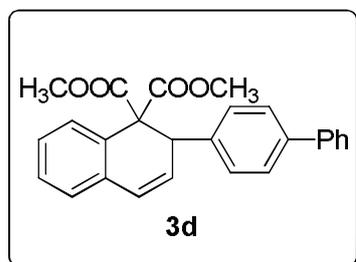
125.4, 63.0, 53.0, 52.1, 46.8. HRMS (ESI) Calcd for $C_{20}H_{18}O_4$: $M+H = 323.1278$.
Found: 323.1284.



dimethyl 2-(p-tolyl)naphthalene-1,1(2H)-dicarboxylate 3b: light yellow solid. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, $J = 7.6$ Hz, 1H), 7.29-7.21(m, 2H), 7.10 (d, $J = 6.8$ Hz, 1H), 6.96-6.92 (m, 4H), 6.49 (d, $J = 10.0$ Hz, 1H), 6.20 (dd, $J = 5.6$ Hz, $J = 9.6$ Hz, 1H), 4.48 (d, $J = 5.6$ Hz, 1H), 3.62 (s, 3H), 3.45 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.1, 169.2, 137.3, 134.2, 133.1, 131.6, 130.0, 129.0, 128.9, 128.7, 128.4, 128.3, 128.3, 127.7, 126.4, 125.2, 62.9, 53.0, 52.0, 46.4, 21.0. HRMS (ESI) Calcd for $C_{21}H_{20}O_4$: $M+H = 337.1434$. Found: 337.1349.

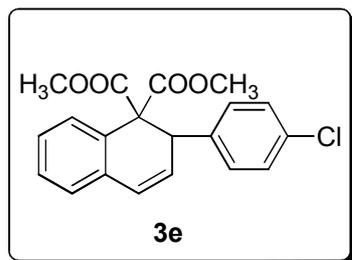


dimethyl 2-(4-methoxyphenyl)naphthalene-1,1(2H)-dicarboxylate 3c: white solid. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, $J = 7.6$ Hz, 1H), 7.30-7.21 (m, 2H), 7.12-7.09 (m, 1H), 6.97 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 8.8$ Hz, 2H), 6.48 (d, $J = 9.6$ Hz, 1H), 6.10 (dd, $J = 6.0$ Hz, $J = 9.6$ Hz, 1H), 4.47 (d, $J = 5.6$ Hz, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.1, 169.3, 159.1, 133.1, 131.7, 130.2, 129.9, 129.3, 128.4, 128.4, 127.7, 126.5, 125.1, 113.6, 63.0, 55.0, 53.0, 52.1, 46.0. HRMS (ESI) Calcd for $C_{21}H_{20}O_5$: $M+H = 353.1384$. Found: 353.1390.

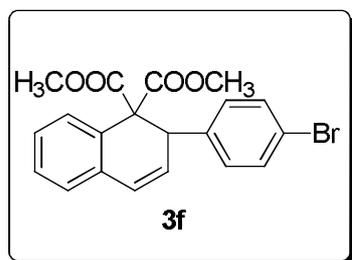


dimethyl 2-([1,1'-biphenyl]-4-yl)naphthalene-1,1(2H)-dicarboxylate 3d: white solid. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, $J = 7.2$ Hz, 1H), 7.51-7.49 (m, 2H), 7.40-7.35 (m, 4H), 7.30-7.22 (m, 3H), 7.15-7.12 (m, 3H), 6.53 (d, $J = 9.6$ Hz, 1H), 6.14 (dd, $J = 5.6$ Hz, $J = 9.6$ Hz, 1H), 4.57 (d, $J = 6.0$ Hz, 1H), 3.65 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.0, 169.3, 140.5, 140.4, 136.5, 133.1, 131.6, 129.9, 129.8, 129.8, 129.3, 129.0, 128.9, 128.6, 128.5, 128.4, 127.8, 127.6,

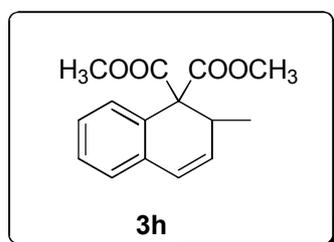
127.2, 127.0, 126.9, 126.9, 126.6, 125.6, 63.0, 53.1, 52.1, 46.5. HRMS (ESI) Calcd for $C_{26}H_{22}O_4$: $M+Na = 421.1410$. Found: 421.1417,



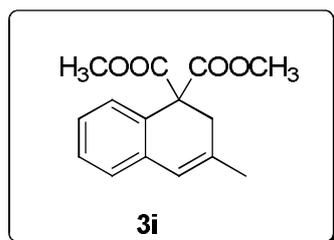
dimethyl 2-(4-chlorophenyl)naphthalene-1,1(2H)-dicarboxylate 3e: light yellow solid. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.54 (d, $J = 7.6$ Hz, 1H), 7.32-7.24 (m, 2H), 7.13-7.11(m, 3H), 6.98(d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 8.4$ Hz, 1H), 6.08 (dd, $J = 6.0$ Hz, $J = 9.6$ Hz, 1H), 4.49 (d, $J = 6.0$ Hz, 1H), 3.64 (s, 3H), 3.47(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.9, 169.2, 136.1, 133.6, 132.8, 131.6, 130.2, 129.6, 129.4, 129.4, 128.9, 128.6, 128.4, 128.2, 127.9, 126.6, 125.8, 62.9, 53.1, 52.2, 46.0. $C_{20}H_{17}ClO_4$: $M+Na = 379.0708$. Found: 379.0715.



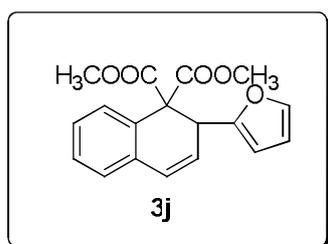
dimethyl 2-(4-bromophenyl)naphthalene-1,1(2H)-dicarboxylate 3f: light yellow solid. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.54-7.52 (m, 1H), 7.31-7.23 (m, 4H), 7.13-7.11(m, 1H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 9.6$ Hz, 1H), 6.07 (dd, $J = 6.0$ Hz, $J = 9.6$ Hz, 1H), 4.48 (d, $J = 5.6$ Hz, 1H), 3.64 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.8, 169.1, 136.6, 132.8, 132.3, 131.6, 131.4, 130.6, 129.9, 129.8, 129.7, 129.3, 129.0, 128.6, 128.2, 127.9, 126.6, 125.8, 121.8, 62.8, 53.1, 52.2, 46.1.



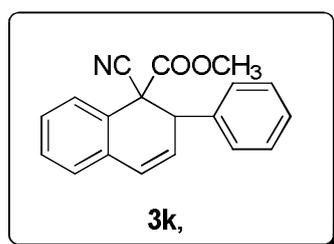
dimethyl 2-methylnaphthalene-1,1(2H)-dicarboxylate 3h: light yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.40 (m, 1H), 7.25-7.22 (m, 2H), 7.05-7.03 (m, 1H), 6.34 (d, $J = 9.2$ Hz, 1H), 5.99 (dd, $J = 5.2$ Hz, $J = 9.6$ Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.35-3.28 (m, 1H), 1.08 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.7, 169.9, 143.2, 132.8, 132.6, 130.4, 130.0, 129.8, 128.9, 128.3, 128.2, 127.3, 126.3, 125.3, 62.8, 52.8, 52.4, 35.1, 15.5. HRMS (ESI) Calcd for $C_{15}H_{16}O_4$: $M+H = 261.1121$. Found: 261.1132.



dimethyl 3-methylnaphthalene-1,1(2H)-dicarboxylate 3i: light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.26-7.22 (m, 1H), 7.19-7.12(m, 2H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.21(s, 1H), 3.75 (s, 6H), 2.93 (s, 2H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.6, 135.5, 134.1, 130.0, 128.4, 128.3, 127.4, 126.5, 125.7, 122.4, 59.8, 53.0, 36.0, 23.0. HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4$: $M+H = 261.1121$. Found: 261.1133.

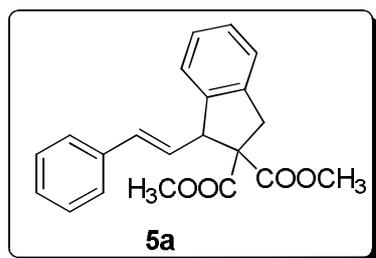


dimethyl 2-(furan-2-yl)naphthalene-1,1(2H)-dicarboxylate 3j: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.42 (m, $J = 7.6$ Hz, 1H), 7.29-7.21 (m, 3H), 7.10 (dd, $J = 1.2$ Hz, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 9.6$ Hz, 1H), 6.21-6.20 (m, 1H), 6.10-6.04 (m, 2H), 4.72 (d, $J = 5.6$ Hz, 1H), 3.68 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 169.8, 169.4, 151.0, 142.2, 132.5, 130.5, 129.2, 128.4, 127.7, 127.1, 126.6, 126.3, 110.4, 108.5, 62.5, 53.1, 52.6, 40.3. HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_5$: $M+H = 313.1071$. Found: 313.1076.

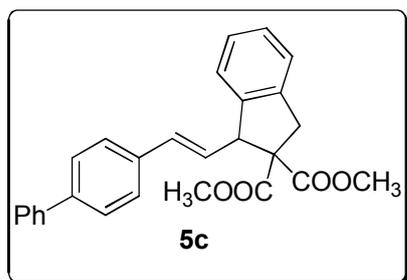


methyl 1-cyano-2-phenyl-1,2-dihydronaphthalene-1-carboxylate 3k: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.38-7.36 (m, 1H), 7.31-7.26 (m, 7H), 7.23 (d, $J = 8.0$ Hz, 1H), 6.72 (dd, $J = 2.0$ Hz, $J = 9.6$ Hz, 1H), 6.11 (dd, $J = 4.4$ Hz, $J = 10.4$ Hz, 1H), 4.47 (dd, $J = 2.0$ Hz, $J = 4.0$ Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 168.2, 136.3, 136.2, 129.8, 129.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.0, 127.6, 127.4, 127.2, 116.8, 53.3, 53.9, 47.3. HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_2$: $M+H = 290.1176$. Found: 290.1181.

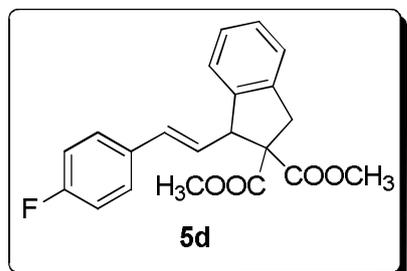
5. Characterization Data of 5a-5j



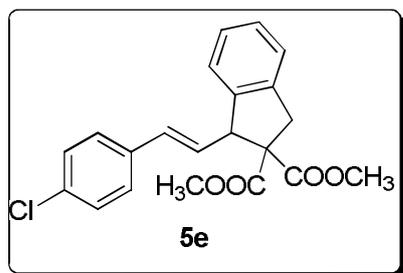
(E)-dimethyl 1-styryl-1H-indene-2,2(3H)-dicarboxylate 5a: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.31 (d, $J = 7.2$ Hz, 2H), 7.28-7.24 (m, 2H), 7.22-7.17 (m, 5H), 6.59 (d, $J = 15.6$ Hz, 1H), 6.08 (dd, $J = 4.2$ Hz, $J = 10.6$ Hz, 1H), 4.78 (d, $J = 9.2$ Hz, 1H), 3.92 (d, $J = 16.8$ Hz, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 3.39 (d, $J = 16.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.7, 170.0, 142.5, 139.3, 136.8, 132.7, 128.5, 127.5, 127.2, 126.4, 124.8, 124.3, 65.4, 54.5, 52.9, 52.5, 39.2. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4$: $M+H = 337.1434$. Found: 337.1449.



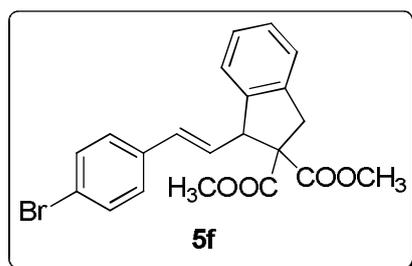
(E)-dimethyl 1-(2-([1,1'-biphenyl]-4-yl)vinyl)-1H-indene-2,2(3H)-dicarboxylate 5c: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.58-7.50 (m, 4H), 7.43-7.38 (m, 4H), 7.33-7.30 (m, 1H), 7.24-7.18 (m, 4H), 6.63 (d, $J = 15.6$ Hz, 1H), 6.13 (dd, $J = 9.6$ Hz, $J = 15.6$ Hz, 1H), 4.81 (d, $J = 9.2$ Hz, 1H), 3.94 (d, $J = 16.8$ Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.41 (d, $J = 16.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.8, 170.1, 142.5, 140.6, 140.3, 139.3, 135.9, 132.3, 128.7, 127.6, 127.3, 127.3, 127.2, 127.2, 127.0, 126.9, 126.8, 124.9, 124.3, 65.5, 54.6, 52.9, 52.6, 39.3.



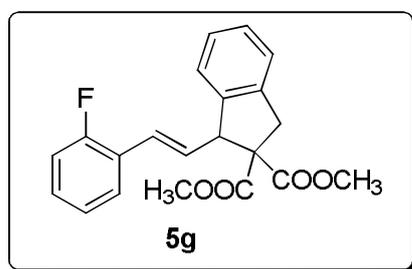
(E)-dimethyl 1-(4-fluorostyryl)-1H-indene-2,2(3H)-dicarboxylate 5d: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.29-7.26 (m, 2H), 7.24-7.16 (m, 4H), 6.98-6.93 (m, 2H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.00 (dd, $J = 9.2$ Hz, $J = 15.6$ Hz, 1H), 4.77 (d, $J = 9.6$ Hz, 1H), 3.91 (d, $J = 16.4$ Hz, 1H), 3.74 (s, 3H), 3.62 (s, 3H), 3.39 (d, $J = 16.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.7, 170.0, 142.4, 139.3, 131.5, 127.9, 127.8, 127.6, 127.2, 127.0, 127.0, 124.8, 124.3, 115.5, 115.3, 65.4, 54.4, 52.9, 52.5, 39.2. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{FO}_4$: $M+H = 355.1340$. Found: 355.1357.



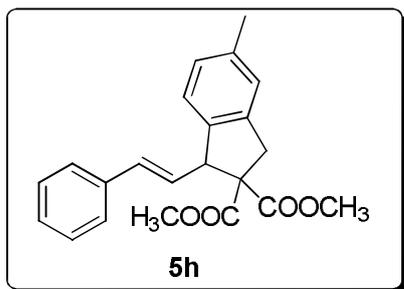
(E)-dimethyl 1-(4-chlorostyryl)-1H-indene-2,2(3H)-dicarboxylate 5e: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.23-7.16 (m, 8H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.07 (dd, $J = 9.2$ Hz, $J = 15.6$ Hz, 1H), 4.77 (d, $J = 9.6$ Hz, 1H), 3.91 (d, $J = 16.4$ Hz, 1H), 3.74 (s, 3H), 3.61 (s, 3H), 3.39 (d, $J = 16.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.6, 170.0, 142.2, 139.3, 135.3, 133.2, 131.5, 128.6, 128.0, 127.6, 127.5, 127.2, 124.8, 124.3, 65.4, 54.4, 52.9, 52.5, 39.2. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{ClO}_4$: $\text{M}+\text{Na} = 393.0867$. Found: 393.0875.



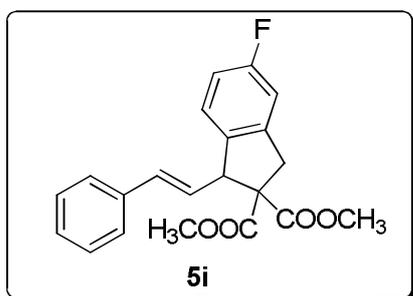
(E)-dimethyl 1-(4-bromostyryl)-1H-indene-2,2(3H)-dicarboxylate 5f: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.39 (d, $J = 8.4$ Hz, 2H), 7.22-7.17 (m, 6H), 6.52 (d, $J = 15.6$ Hz, 1H), 6.08 (dd, $J = 9.6$ Hz, $J = 13.2$ Hz, 1H), 4.77 (d, $J = 9.2$ Hz, 1H), 3.91 (d, $J = 16.8$ Hz, 1H), 3.74 (s, 3H), 3.62 (s, 3H), 3.39 (d, $J = 16.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.6, 170.0, 142.2, 139.3, 135.7, 131.6, 131.5, 128.1, 127.6, 127.2, 124.8, 124.4, 121.3, 65.4, 54.4, 52.9, 52.5, 39.2. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{BrO}_4$: $\text{M}+\text{Na} = 437.0359$. Found: 437.0362.



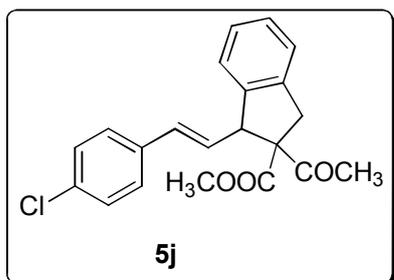
(E)-dimethyl 1-(2-fluorostyryl)-1H-indene-2,2(3H)-dicarboxylate 5g: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.37 -7.33 (m, 1H), 7.24-7.14 (m, 5H), 7.05-6.97 (m, 2H), 6.75 (d, $J = 15.6$ Hz, 1H), 6.15 (dd, $J = 9.6$ Hz, $J = 16.0$ Hz, 1H), 4.80 (d, $J = 9.6$ Hz, 1H), 3.92 (d, $J = 16.4$ Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 3.40 (d, $J = 16.4$ Hz, 1H). ^{13}C NMR (400 MHz, CDCl_3) 171.7, 170.0, 142.3, 139.3, 130.0, 129.9, 128.8, 128.8, 127.6, 127.5, 127.5, 127.2, 125.3, 125.2, 124.8, 124.7, 124.6, 124.3, 124.0, 124.0, 115.7, 115.5, 65.5, 54.9, 52.9, 52.5, 39.2. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{FO}_4$: $\text{M}+\text{H} = 355.1340$. Found: 355.1342.



(E)-dimethyl 5-methyl-1-styryl-1H-indene-2,2(3H)-dicarboxylate 5h: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.32-7.30 (m, 2H), 7.27-7.22 (m, 2H), 7.21-7.16 (m, 1H), 7.07-7.04 (m, 2H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.07 (dd, $J = 9.2$ Hz, $J = 15.6$ Hz, 1H), 3.88 (d, $J = 16.4$ Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 3.35 (d, $J = 16.8$ Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (400 MHz, CDCl_3) 171.7, 170.1, 139.5, 139.4, 137.2, 136.9, 132.5, 128.4, 128.3, 128.0, 127.4, 126.3, 124.9, 124.5, 65.6, 54.1, 52.8, 52.4, 39.1, 22.6, 21.2. HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4$: $\text{M}+\text{H} = 351.1591$. Found: 351.1607.



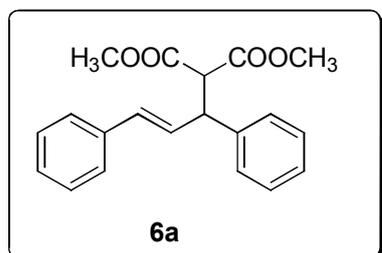
(E)-dimethyl 5-fluoro-1-styryl-1H-indene-2,2(3H)-dicarboxylate 5i: light yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.32-7.25 (m, 4H), 7.24-7.18 (m, 1H), 7.12-7.09 (m, 1H), 6.92-6.85 (m, 2H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.06 (dd, $J = 9.2$ Hz, $J = 15.6$ Hz, 1H), 4.73 (d, $J = 9.2$ Hz, 1H), 3.89 (d, $J = 16.8$ Hz, 1H), 3.74 (s, 3H), 3.62 (s, 3H), 3.36 (d, $J = 17.2$ Hz, 1H). ^{13}C NMR (400 MHz, CDCl_3) 171.5, 169.8, 141.5, 141.4, 138.0, 138.0, 136.7, 132.9, 128.5, 127.6, 126.9, 126.3, 126.0, 125.9, 115.5, 114.3, 114.1, 111.5, 111.3, 65.8, 53.7, 52.9, 52.5, 39.1. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{FO}_4$: $\text{M}+\text{H} = 355.1340$. Found: 355.1357.



(E)-methyl 2-acetyl-1-(4-chlorostyryl)-2,3-dihydro-1H-indene-2-carboxylate 5j: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.26-7.19 (m, 8H), [6.65 (d), 6.54 (d), $J = 15.6$ Hz, 1H)], [6.10 (dd), 5.98 (dd), $J = 9.6$ Hz, $J = 16.0$ Hz, 1H)], 4.83-4.78 (m, 1H), 3.93 (d, $J = 16.8$ Hz, 1H), [3.78 (s), 3.65 (s), 3H], 3.33-3.25 (m, 1H), [2.27 (s),

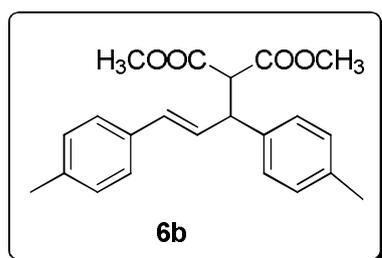
2.15 (s, 3H). ^{13}C NMR (400 MHz, CDCl_3) 201.8, 172.7, 170.8, 142.5, 142.1, 139.4, 138.7, 135.3, 135.0, 133.3, 133.1, 131.4, 128.6, 128.4, 127.7, 127.6, 127.6, 127.5, 127.3, 127.2, 124.8, 124.7, 124.5, 124.4, 71.7, 71.5, 54.2, 52.9, 52.7, 52.4, 38.1, 37.5, 28.1, 26.6. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{ClO}_3$: $\text{M}+\text{Na} = 377.0915$. Found: 377.0922.

6. Characterization Data of 6a-6j

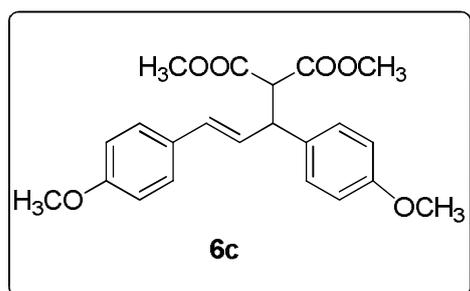


(E)-dimethyl 2-(1,3-diphenylallyl)malonate 6a: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.32-7.16 (m, 10H), 6.48 (d, $J = 15.6$ Hz, 1H), 6.33 (dd, $J = 8.4$ Hz, $J = 15.6$ Hz, 1H), 4.27 (dd, $J = 8.8$ Hz, $J = 10.8$ Hz, 1H), 3.96 (d, $J = 10.8$ Hz, 1H), 3.69 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (400 MHz, CDCl_3) 168.1, 167.7, 140.1, 136.7, 131.8, 129.1, 128.6, 128.4, 127.8, 127.5, 127.1, 126.3, 57.6, 52.5, 52.4, 49.1. HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$: $\text{M}+\text{H} = 325.1434$. Found: 325.1250

The data match with the previous report.⁴

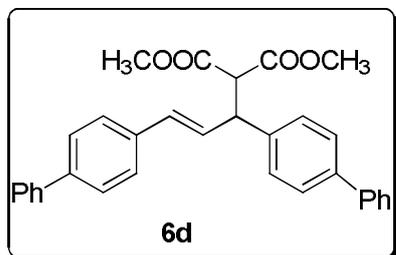


(E)-dimethyl 2-(1,3-di-p-tolylallyl)malonate 6b: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.20-7.16 (m, 4H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.26 (dd, $J = 8.4$ Hz, $J = 15.6$ Hz, 1H), 4.24-4.19 (m, 1H), 3.93 (d, $J = 10.8$ Hz, 1H), 3.67 (s, 3H), 3.51 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (400 MHz, CDCl_3) 168.2, 167.8, 137.2, 136.6, 134.0, 131.4, 129.3, 129.0, 128.2, 127.6, 126.2, 57.7, 52.4, 52.3, 48.8, 21.0, 20.9. HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4$: $\text{M}+\text{Na} = 375.1567$. Found: 375.1571.

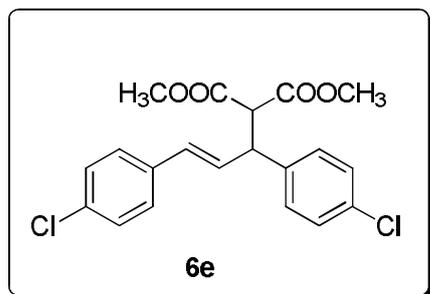


(E)-dimethyl 2-(1,3-bis(4-methoxyphenyl)allyl)malonate 6c: light yellow oil. ^1H

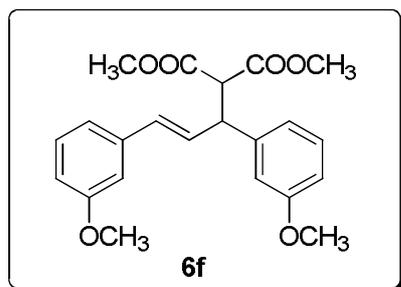
NMR (400 MHz, CDCl₃) 7.24-7.19 (m, 4H), 6.85-6.78 (m, 4H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 8.8 Hz, *J* = 16.0 Hz, 1H), 4.22-4.18 (m, 1H), 3.90 (d, *J* = 10.8 Hz, 1H), 3.75 (s, 6H), 3.68 (s, 3H), 3.51 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) 168.1, 167.8, 159.0, 158.4, 132.3, 130.8, 129.5, 128.7, 127.4, 127.1, 113.9, 113.7, 57.8, 55.1, 55.0, 52.4, 52.2, 48.3. HRMS (ESI) Calcd for C₂₂H₂₄O₆: M+Na = 407.1465. Found: 407.1462.



(E)-dimethyl 2-(1,3-di([1,1'-biphenyl]-4-yl)allyl)malonate 6d: light yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.55 (d, *J* = 6.0 Hz, 6H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 8H), 7.31 (d, *J* = 6.8 Hz, 2H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.41 (dd, *J* = 8.4 Hz, *J* = 15.6 Hz, 1H), 4.38-4.33 (m, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) 168.1, 167.7, 140.5, 140.3, 139.9, 139.2, 135.8, 131.4, 129.0, 128.7, 128.5, 128.2, 128.1, 127.4, 127.2, 127.1, 126.9, 126.8, 126.8, 57.5, 52.6, 52.4, 48.8.

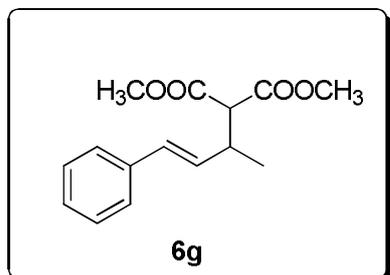


(E)-dimethyl 2-(1,3-bis(4-chlorophenyl)allyl)malonate 6e: light yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.30-7.21 (m, 8H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.26 (dd, *J* = 8.4 Hz, *J* = 16.0 Hz, 1H), 4.24 (dd, *J* = 8.8 Hz, *J* = 10.8 Hz, 1H), 3.90 (d, *J* = 10.8 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) 167.9, 167.5, 138.5, 135.0, 133.4, 133.1, 131.0, 129.2, 129.2, 128.9, 128.7, 127.6, 57.3, 52.7, 52.6, 48.4. C₂₀H₁₈Cl₂O₄: M+H = 393.0655. Found: 393.0646.

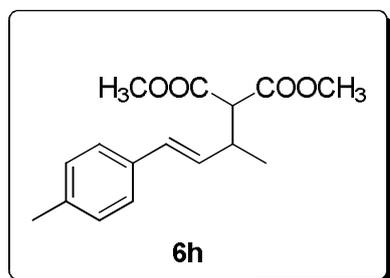


(E)-dimethyl 2-(1,3-bis(3-methoxyphenyl)allyl)malonate 6f: light yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.24-7.16 (m, 2H), 6.92-6.87 (m, 2H), 6.84 (d, *J* = 2.0 Hz,

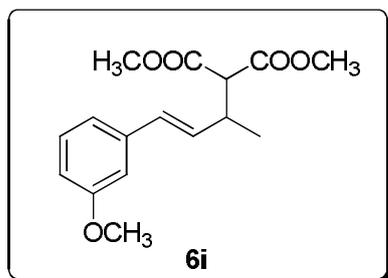
2H), 6.77-6.74 (m, 2H), 6.45 (d, $J = 15.6$ Hz, 1H), 6.30 (dd, $J = 8.8$ Hz, $J = 15.6$ Hz, 1H), 4.23 (dd, $J = 8.8$ Hz, $J = 10.8$ Hz, 1H), 3.95 (d, $J = 10.8$ Hz, 1H), 3.77 (d, $J = 2.8$ Hz, 6H), 3.69 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (400 MHz, CDCl_3) 168.1, 167.6, 159.7, 159.7, 141.7, 138.2, 131.7, 129.6, 129.4, 129.2, 120.0, 119.0, 113.7, 113.1, 112.3, 111.7, 57.4, 55.1, 55.1, 52.5, 52.4, 49.1. HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_6$: $\text{M}+\text{H} = 385.1646$. Found: 385.1662.



(E)-dimethyl 2-(4-phenylbut-3-en-2-yl)malonate 6g: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.34-7.25 (m, 4H), 7.22-7.19 (m, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.12 (dd, $J = 8.4$ Hz, $J = 15.6$ Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.40 (d, $J = 8.8$ Hz, 1H), 3.17-3.08 (m, 1H), 1.90 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (400 MHz, CDCl_3) 168.6, 168.5, 137.0, 131.1, 130.8, 128.4, 127.3, 126.2, 57.7, 52.4, 52.3, 37.7, 18.4.

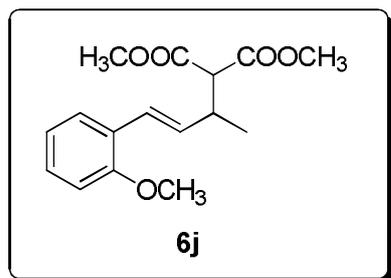


(E)-dimethyl 2-(4-(p-tolyl)but-3-en-2-yl)malonate 6h: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.22 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 7.6$ Hz, 2H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.06 (dd, $J = 8.4$ Hz, $J = 15.8$ Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.39 (d, $J = 9.2$ Hz, 1H), 3.15-3.06 (m, 1H), 2.31 (s, 3H), 1.18 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (400 MHz, CDCl_3) 168.6, 168.6, 137.1, 134.3, 130.6, 130.1, 129.1, 126.1, 57.8, 52.3, 52.2, 37.7, 21.1, 18.4. HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4$: $\text{M}+\text{Na} = 299.1254$. Found: 299.1258.



(E)-dimethyl 2-(4-(3-methoxyphenyl)but-3-en-2-yl)malonate 6i: light yellow oil. ^1H NMR (400 MHz, CDCl_3) 7.22-7.18 (m, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.87-6.86 (m, 1H), 6.77 (dd, $J = 2.4$ Hz, $J = 8.0$ Hz, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.12 (dd, $J = 8.4$ Hz, $J = 15.6$ Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.67 (s, 3H), 3.40 (d, $J = 8.4$ Hz, 1H), 3.17-3.07 (m, 1H), 1.19 (d, $J = 6.8$ Hz, 1H). ^{13}C NMR (400 MHz, CDCl_3) 168.5,

168.5, 159.7, 138.5, 131.4, 130.7, 129.4, 118.8, 112.9, 111.6, 57.7, 55.1, 52.3, 52.3, 37.6, 18.4. HRMS (ESI) Calcd for C₁₆H₂₀O₅: M+H = 293.1384. Found: 293.1380.

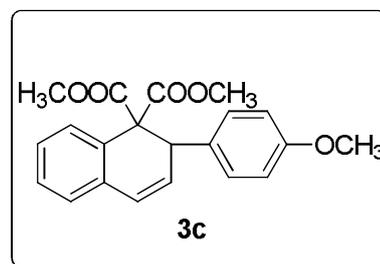
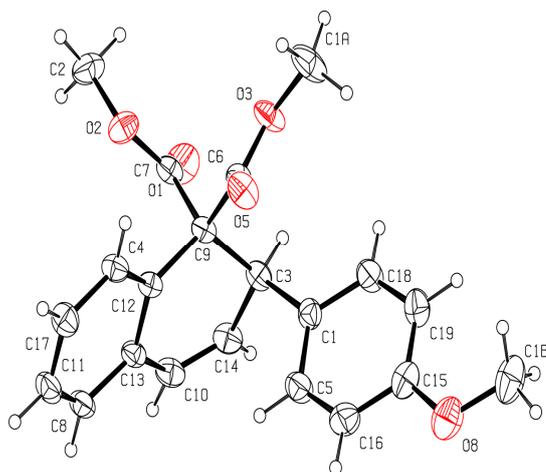


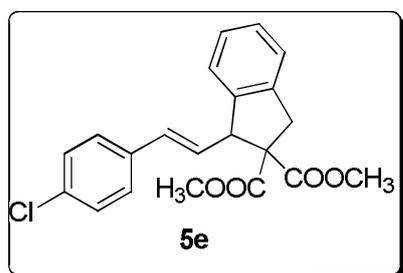
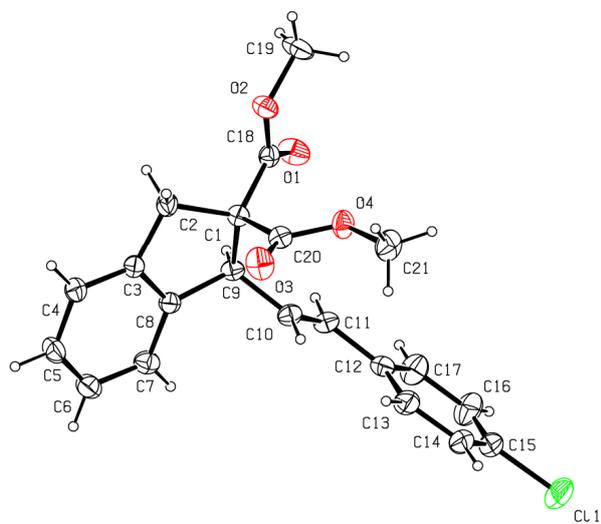
(E)-dimethyl 2-(4-(2-methoxyphenyl)but-3-en-2-yl)malonate 6j: light yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.37 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 6.91-6.87 (m, 1H), 6.84-6.76 (m, 2H), 6.10 (dd, *J* = 8.4 Hz, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.67 (s, 3H), 3.41 (d, *J* = 8.8 Hz, 1H), 3.18-3.09 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) 168.7, 168.6, 156.5, 131.6, 128.4, 126.6, 126.2, 125.5, 120.5, 110.7, 57.9, 55.3, 52.3, 52.2, 38.0, 18.5. HRMS (ESI) Calcd for C₁₆H₂₀O₅: M+H = 293.1384. Found: 293.1391.

7. References

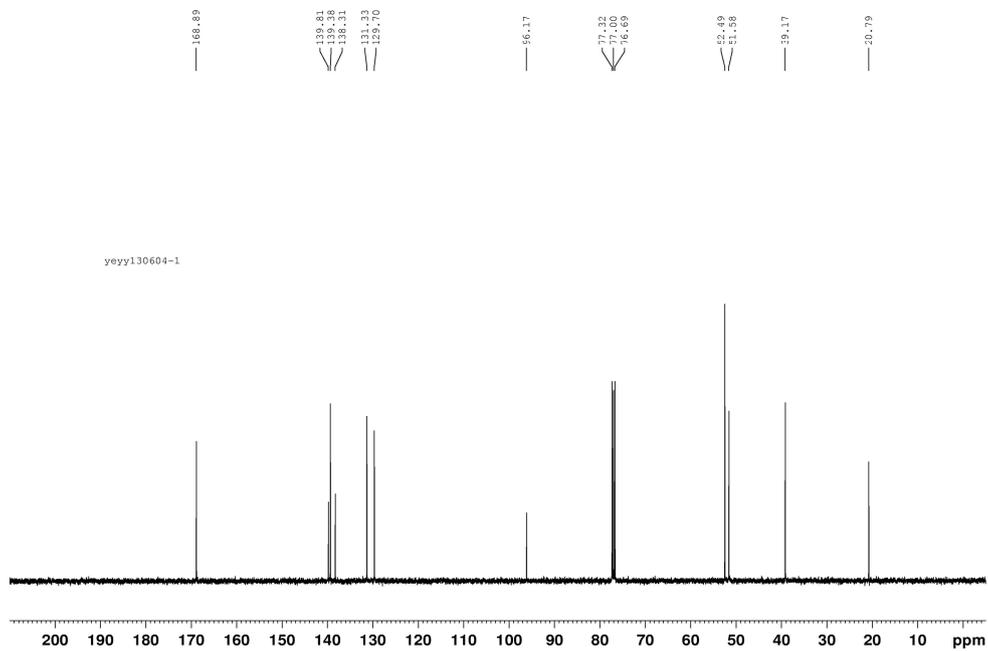
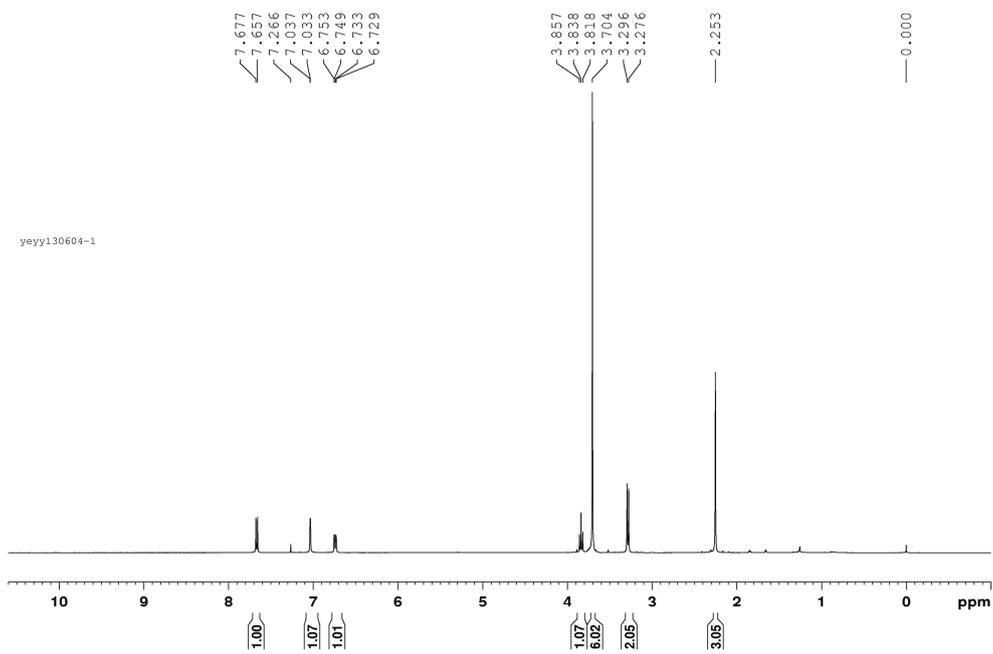
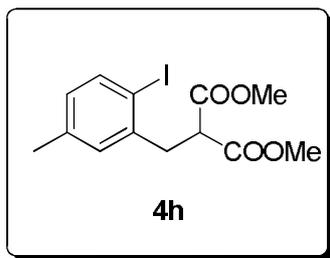
- 1) D. Zhang, E. K. Yum, Z. Liu and R. C. Larock, *Org. Lett.*, 2005, **7**, 4963.
- 2) P.-X. Zhou, J.-Y. Luo, L.-B. Zhao, Y.-Y. Ye and Y.-M. Liang, *Chem. Commun.*, 2013, **49**, 3252.
- 3) H.-P. Bi, L.-N. Guo, X.-H. Duan, F.-R. Gou, S.-H. Huang, X.-Y. Liu and Y.-M. Liang, *Org. Lett.*, 2007, **9**, 397.
- 4) R. Šebesta, A. Škvorcová and B. Horváth, *Tetrahedron: Asymmetry*, 2010, **21**, 1910.

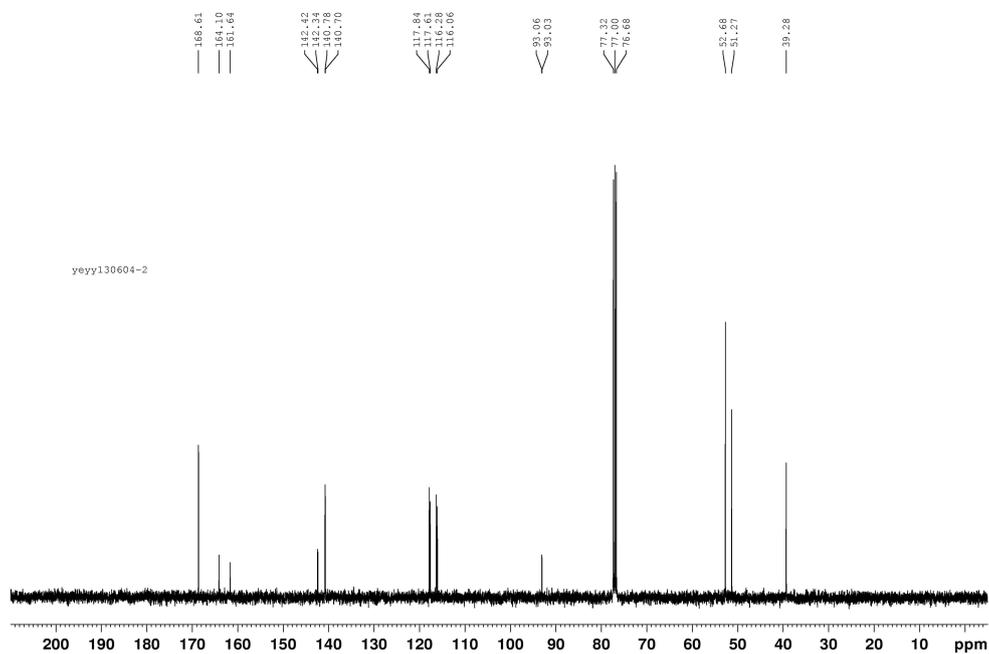
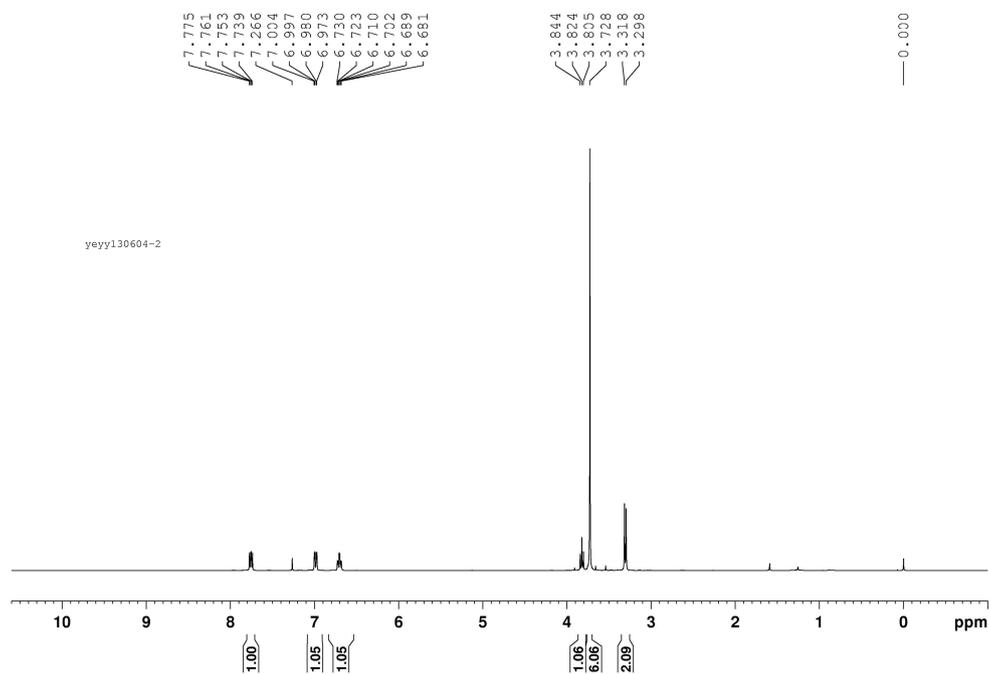
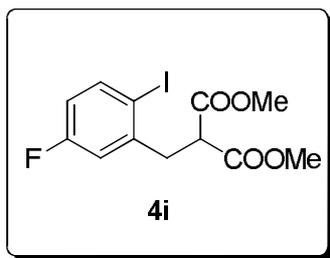
8. The crystal structure of product 3c and 5e

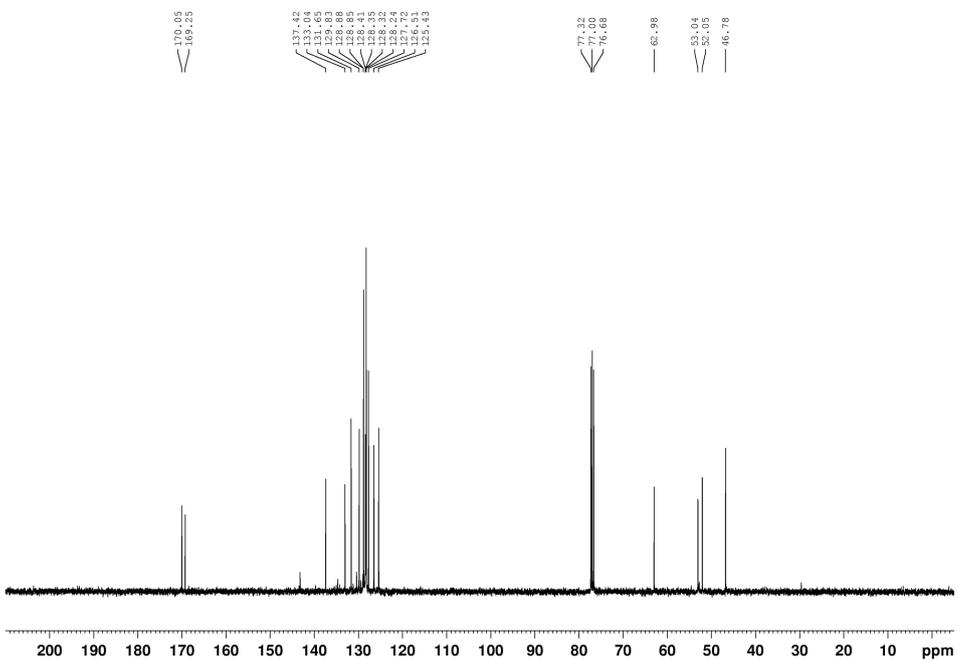
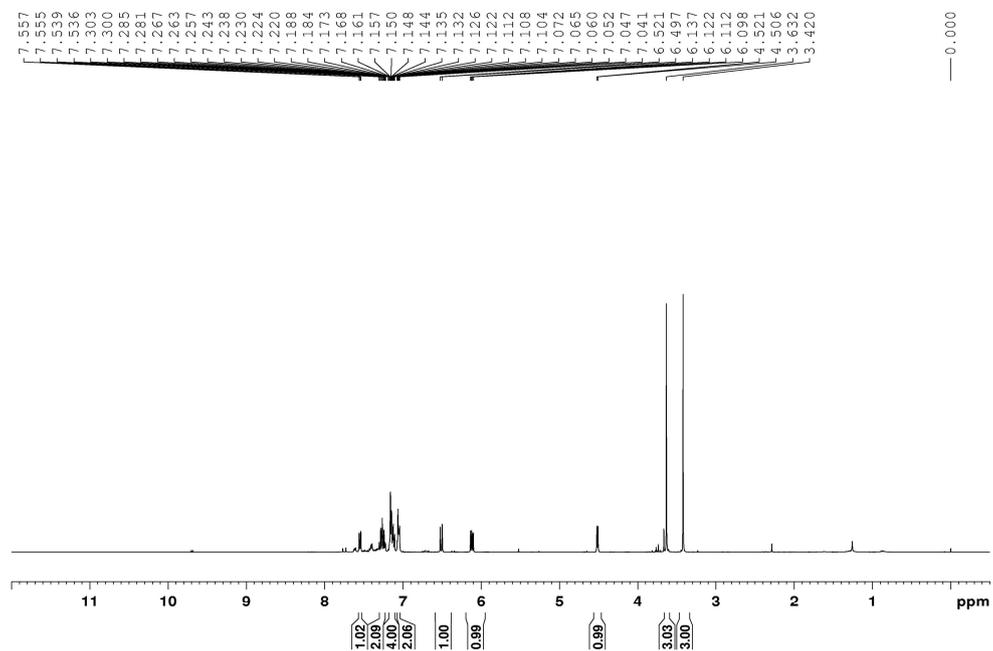
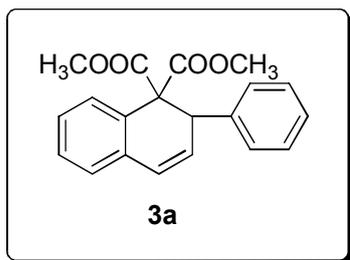


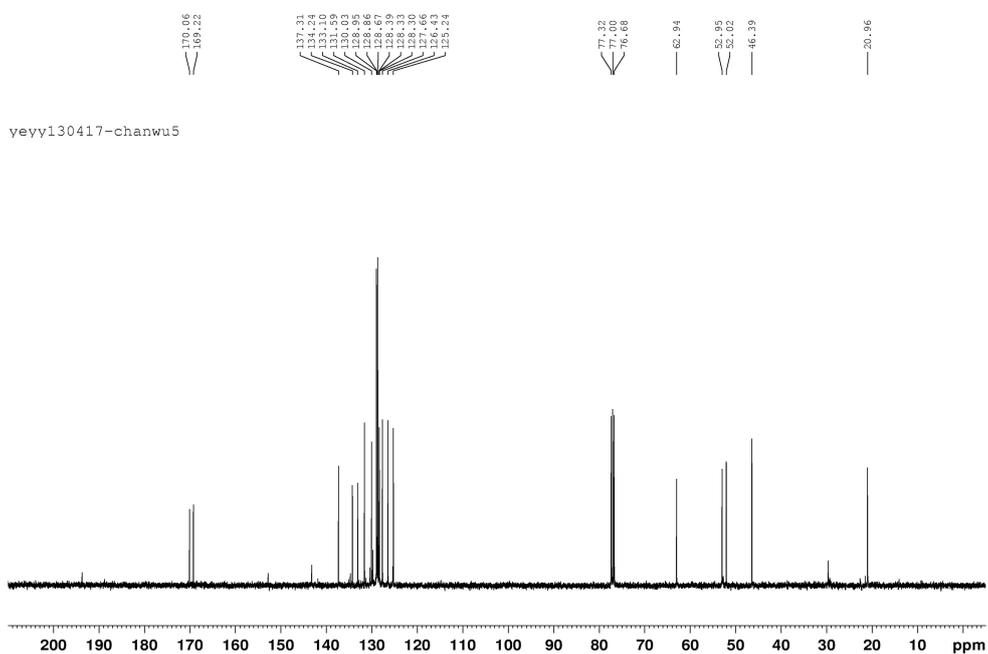
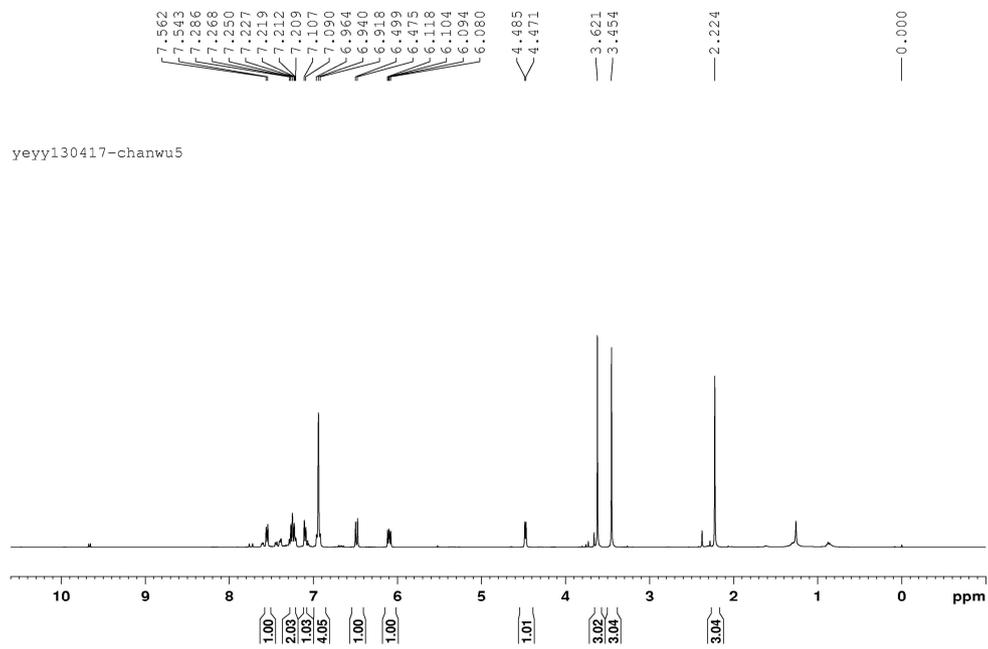
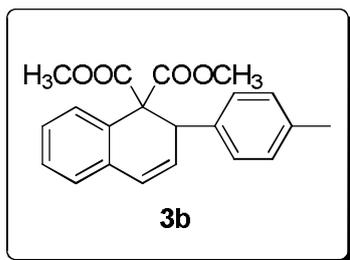


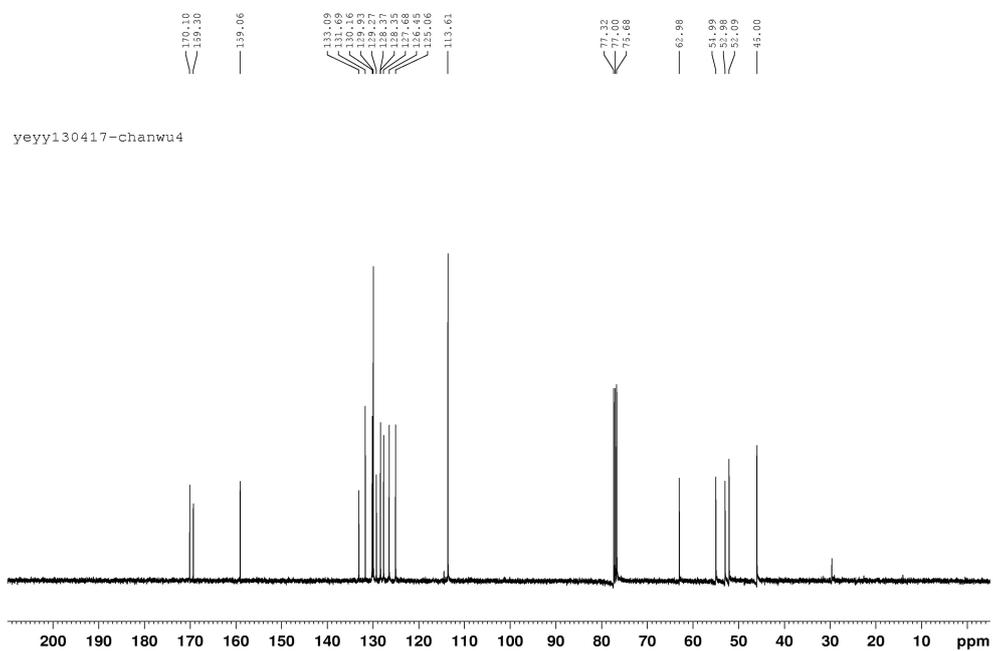
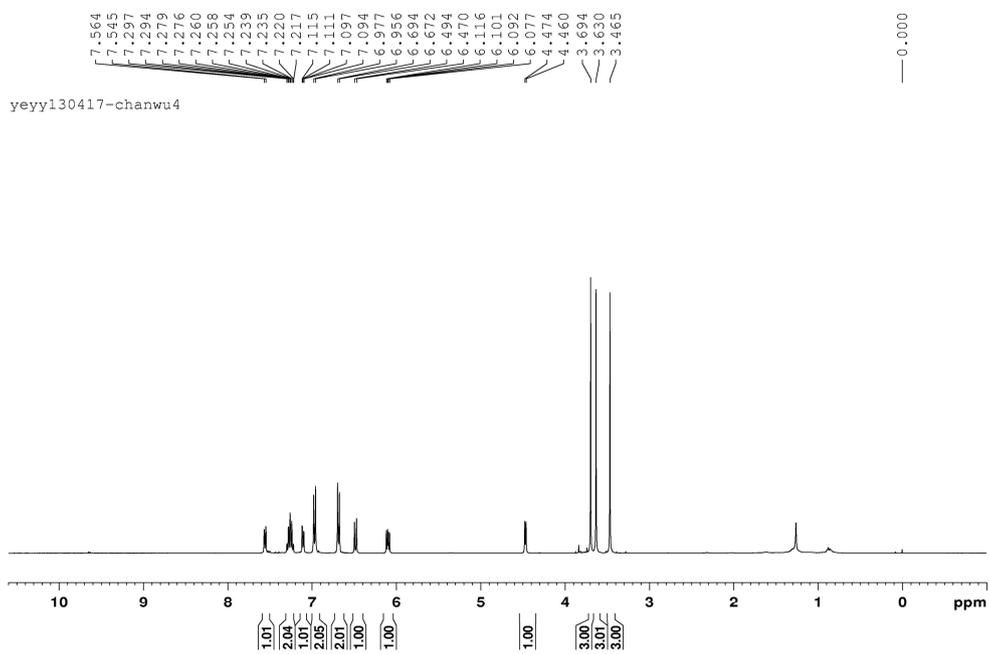
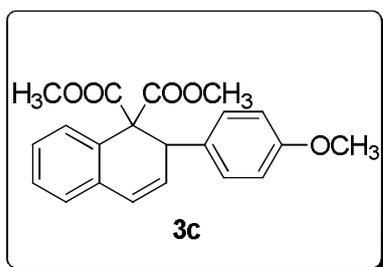
9. ¹H NMR and ¹³C NMR Spectra for Products

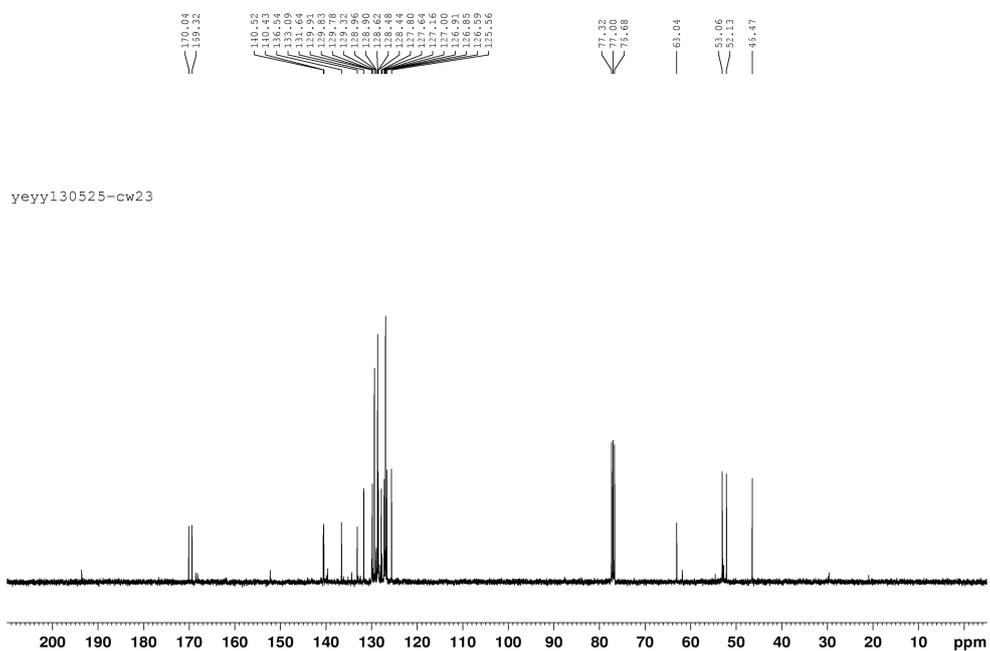
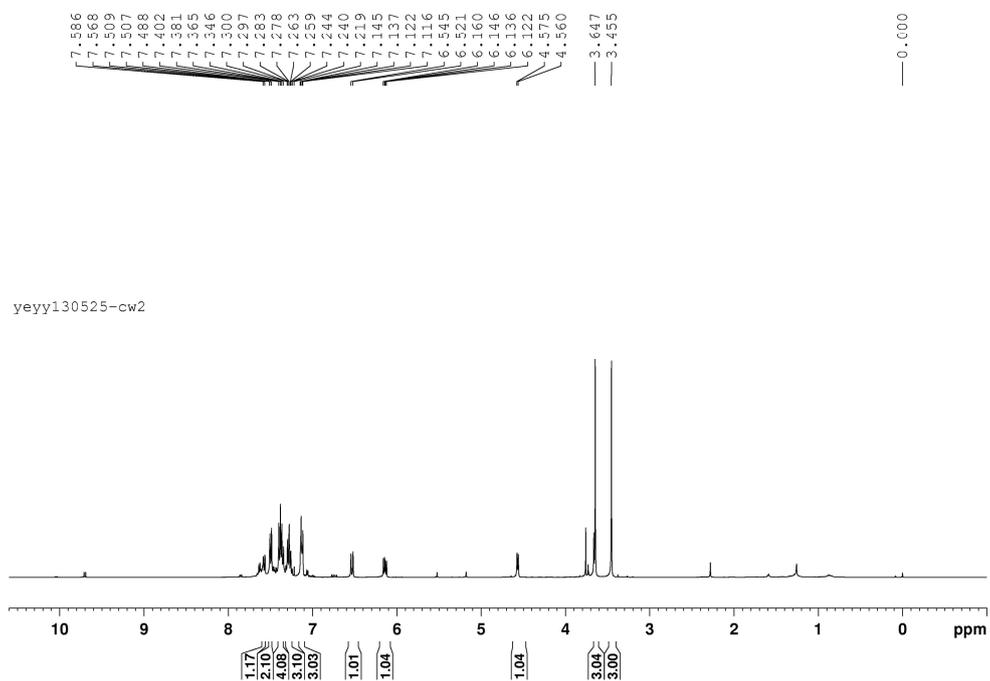
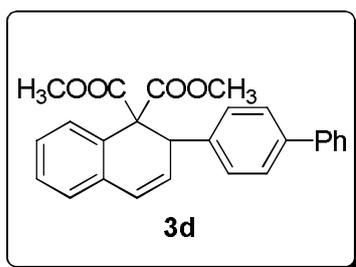


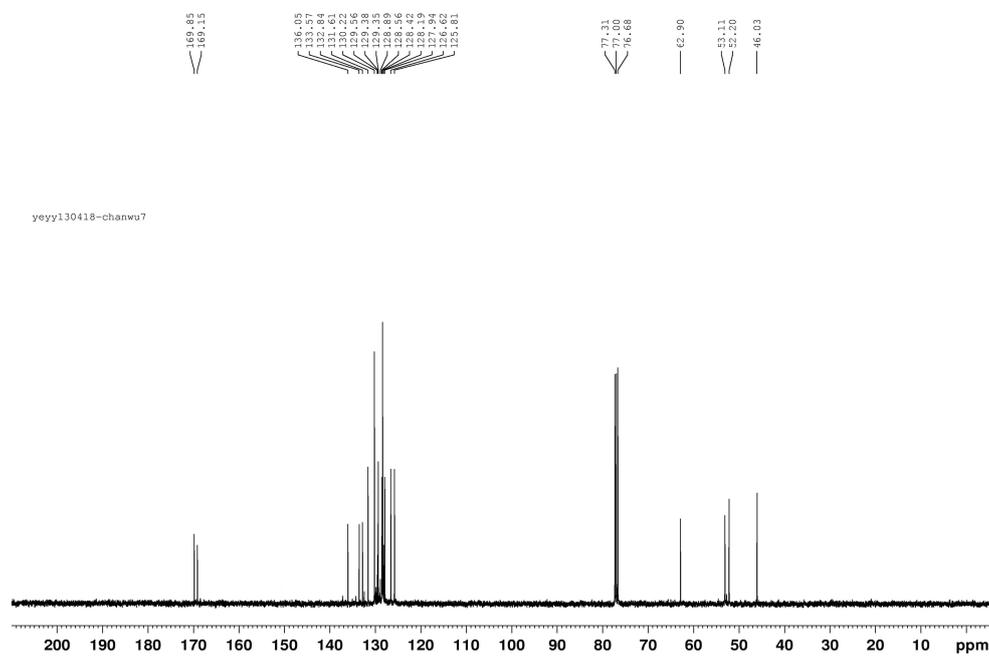
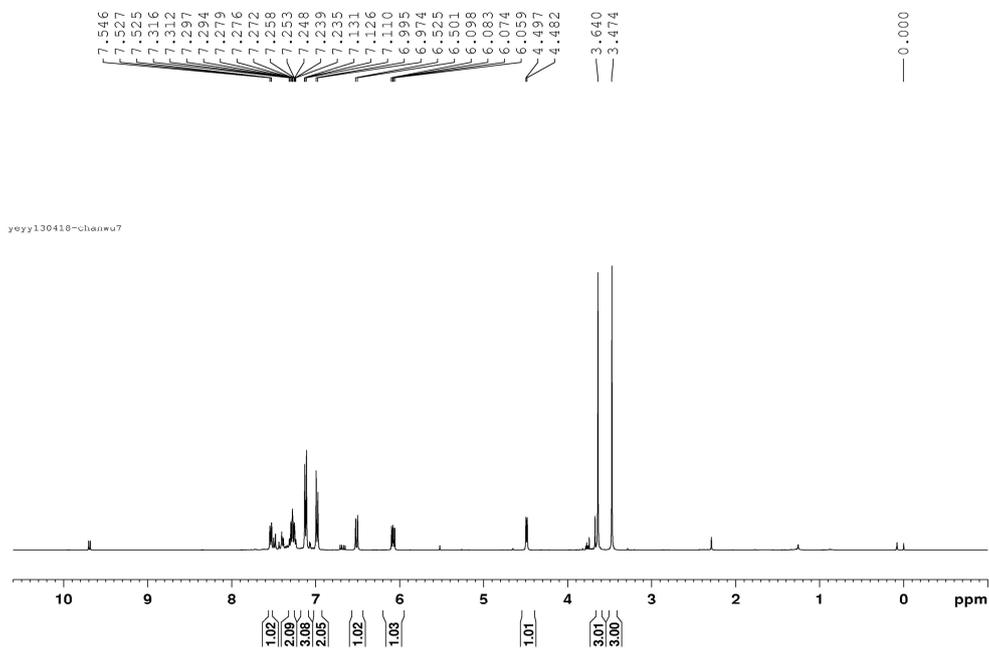
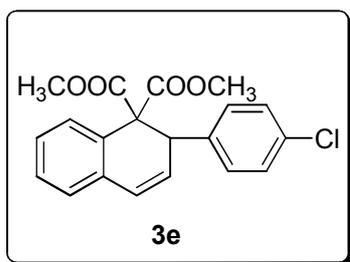


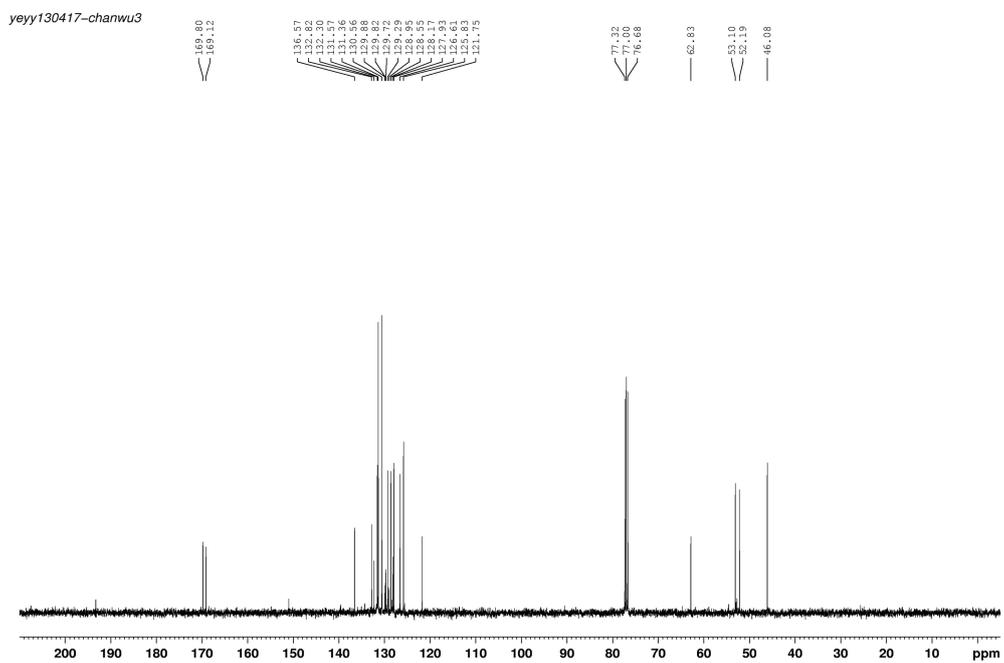
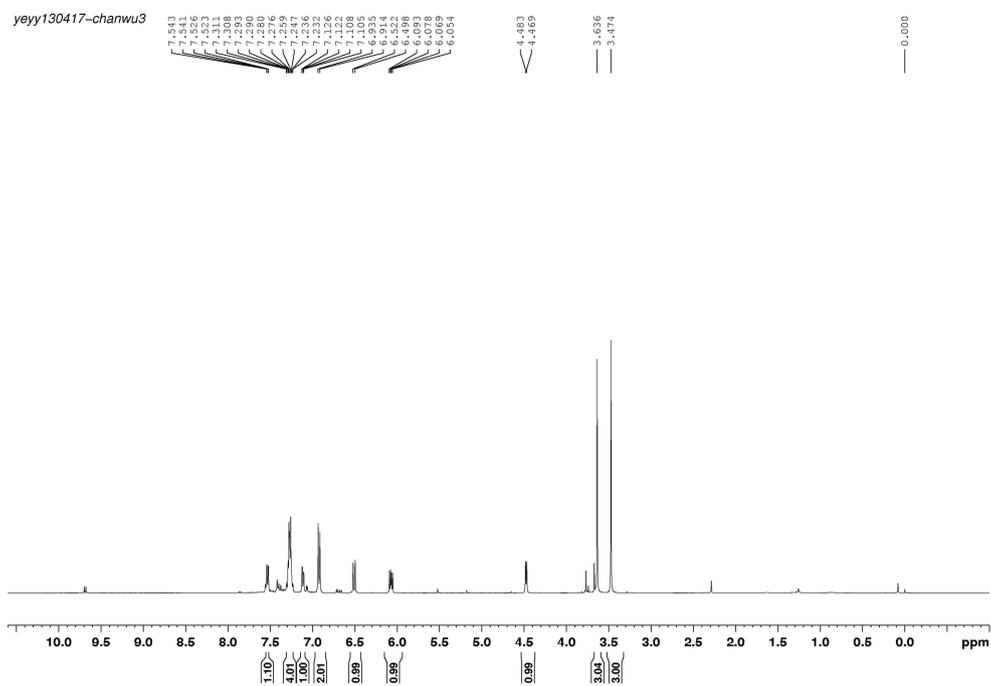
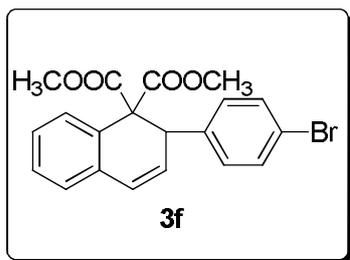


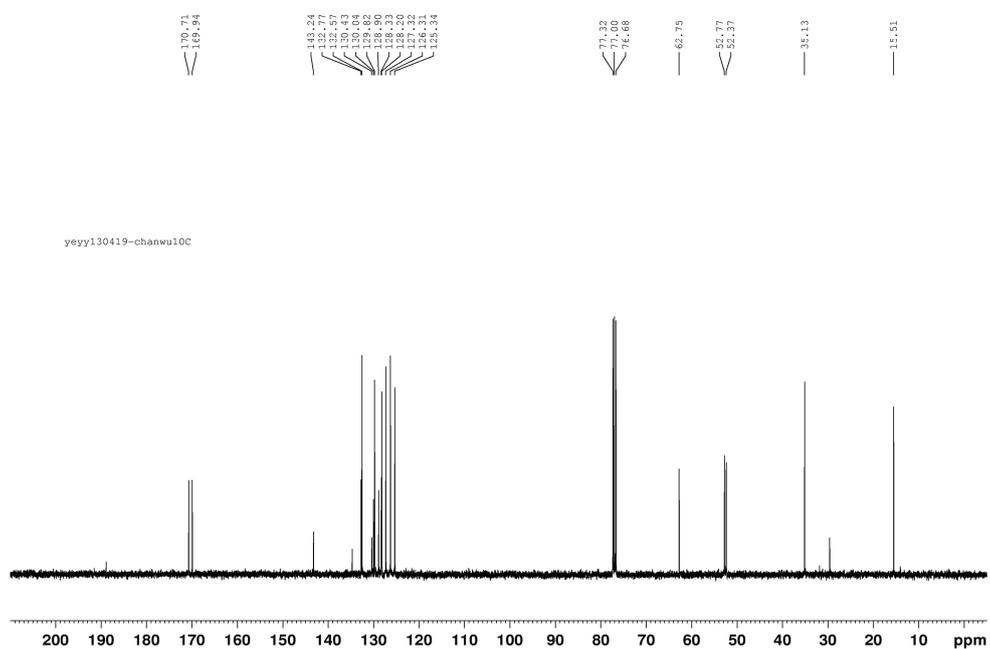
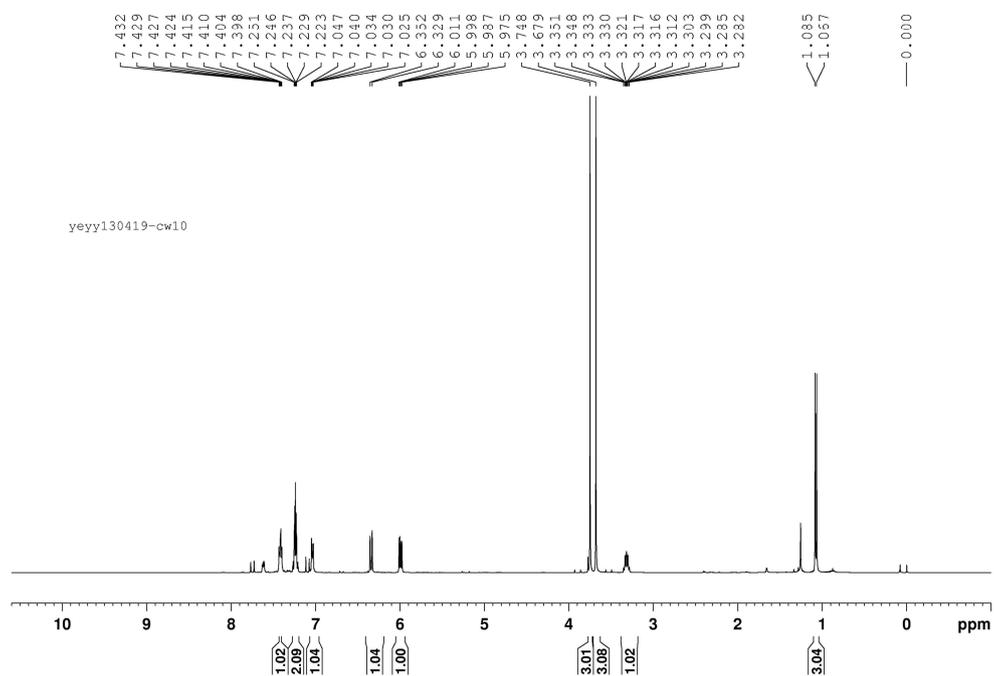
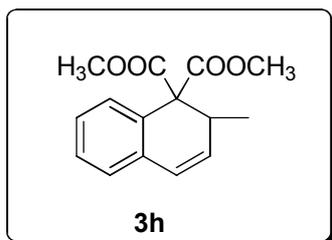


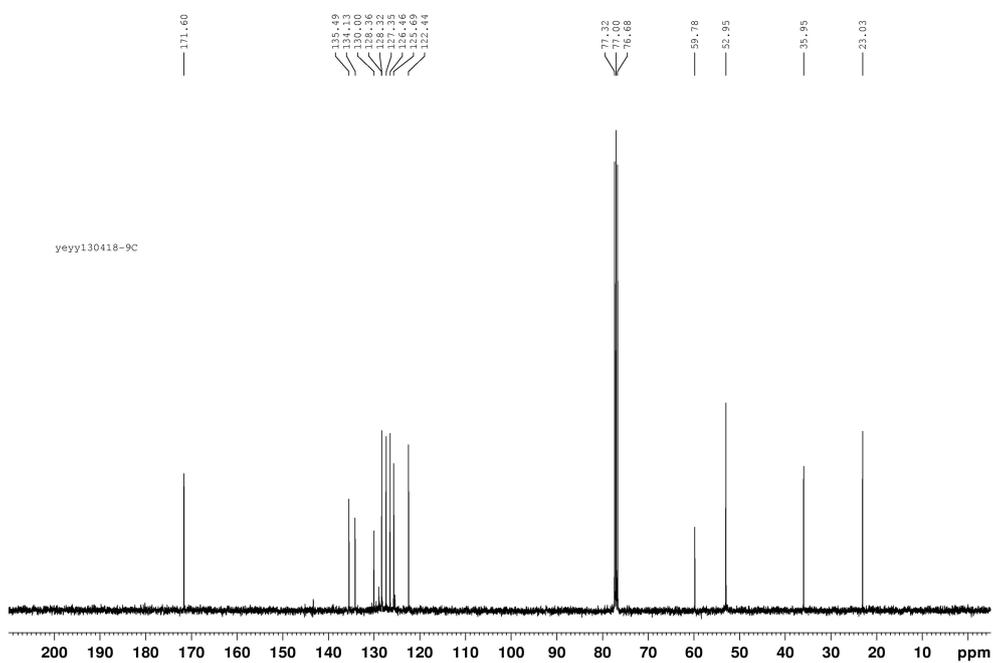
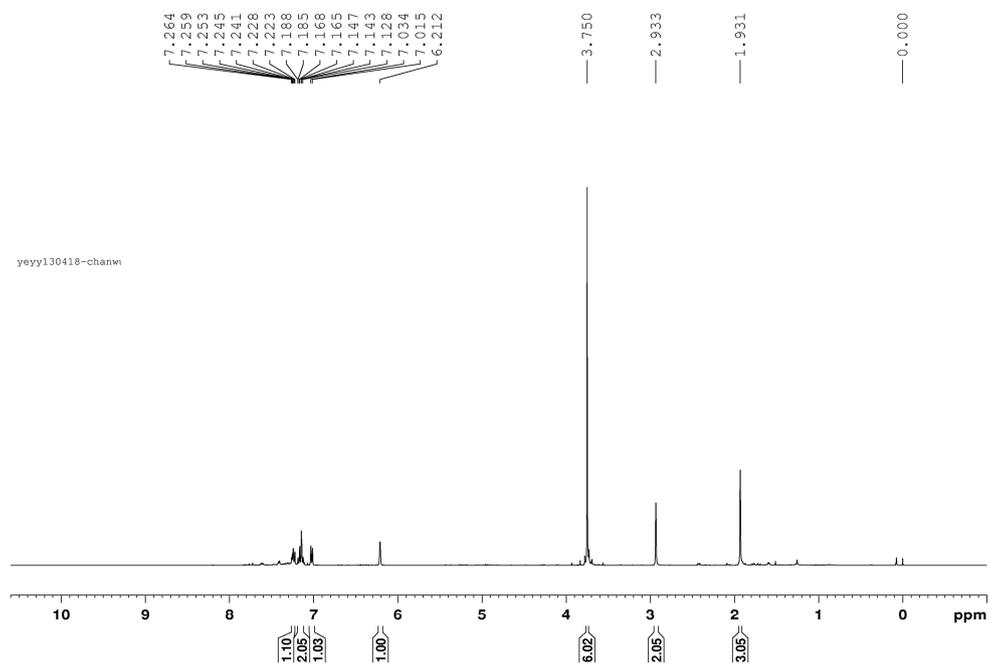
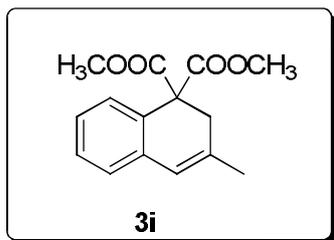


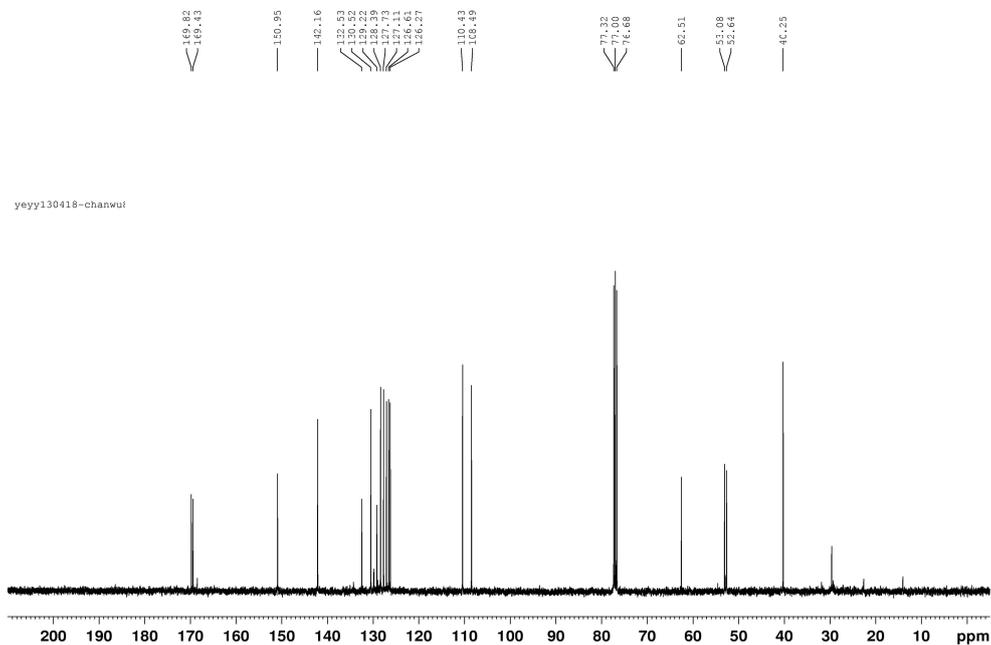
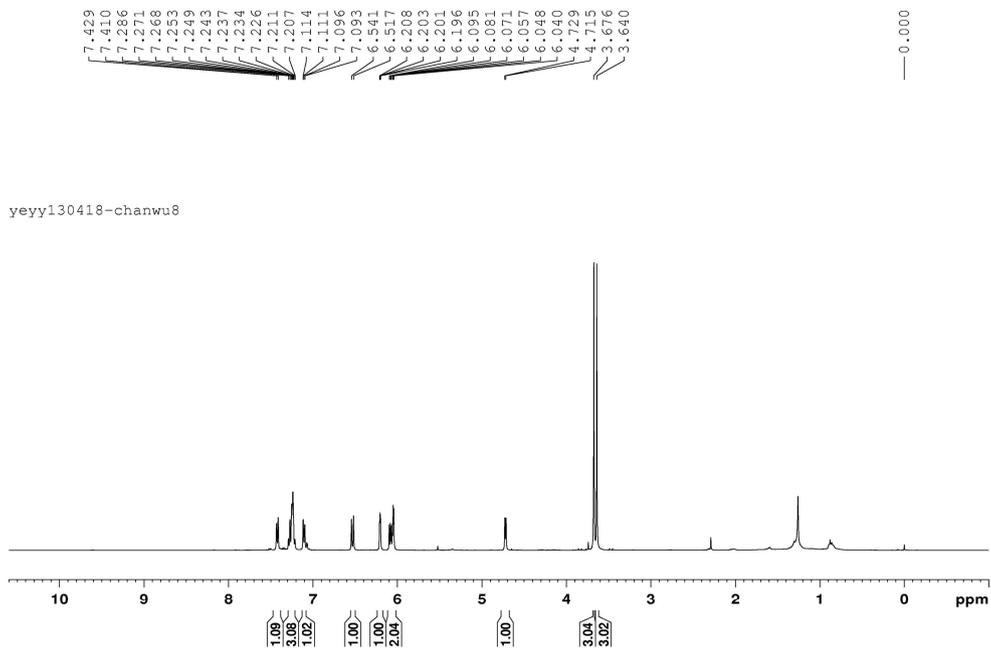
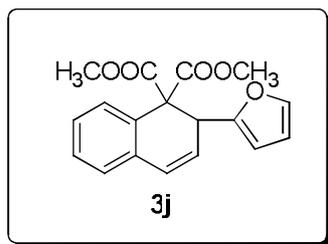


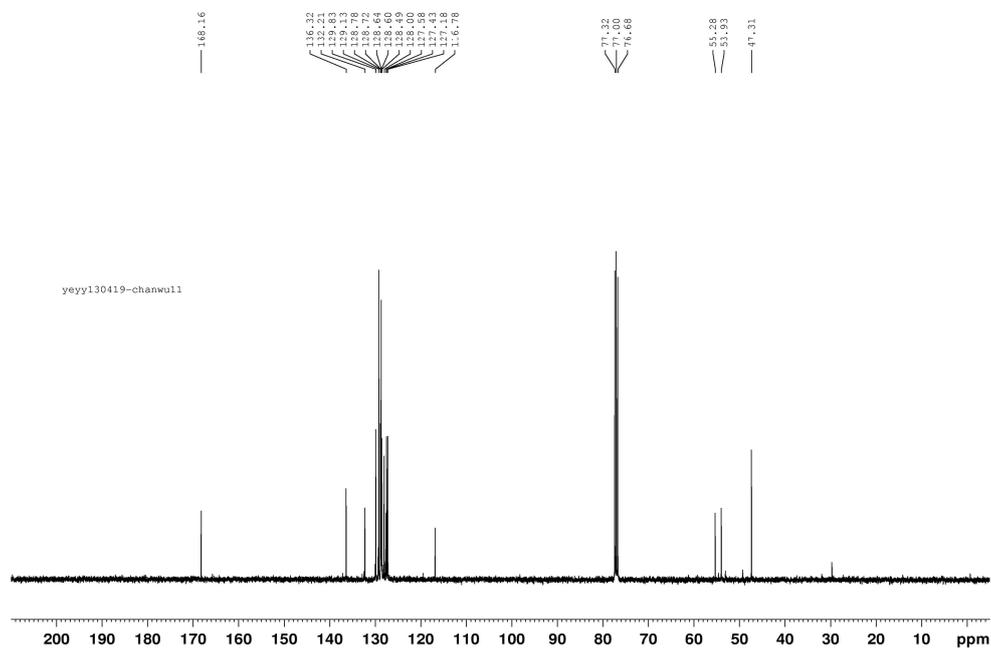
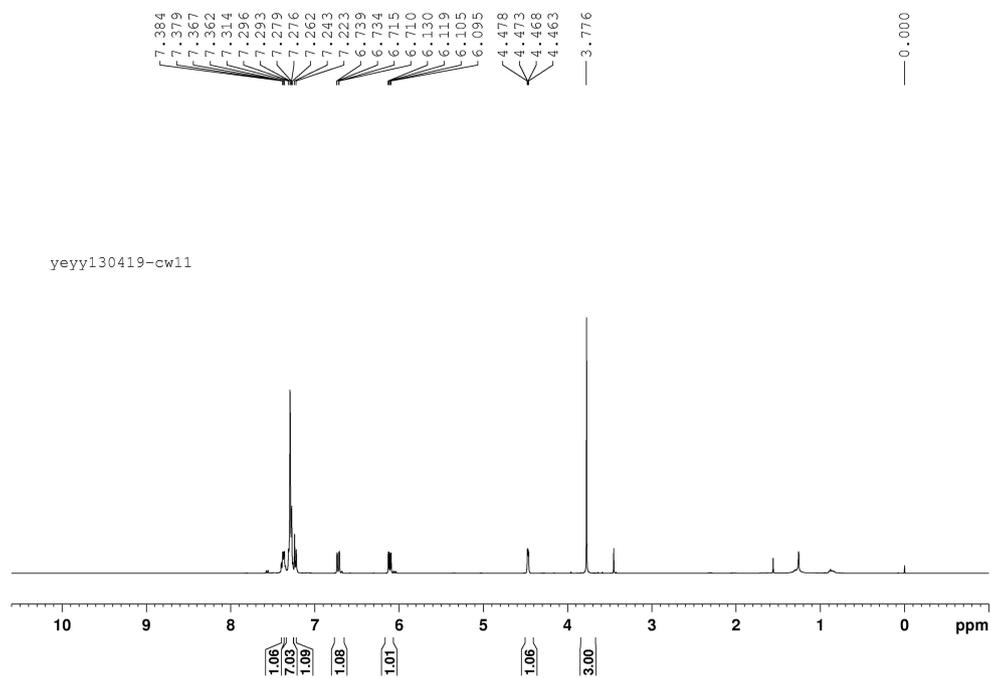
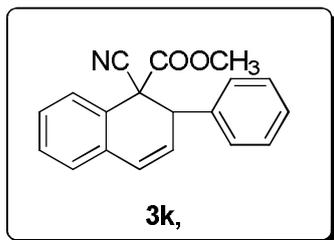


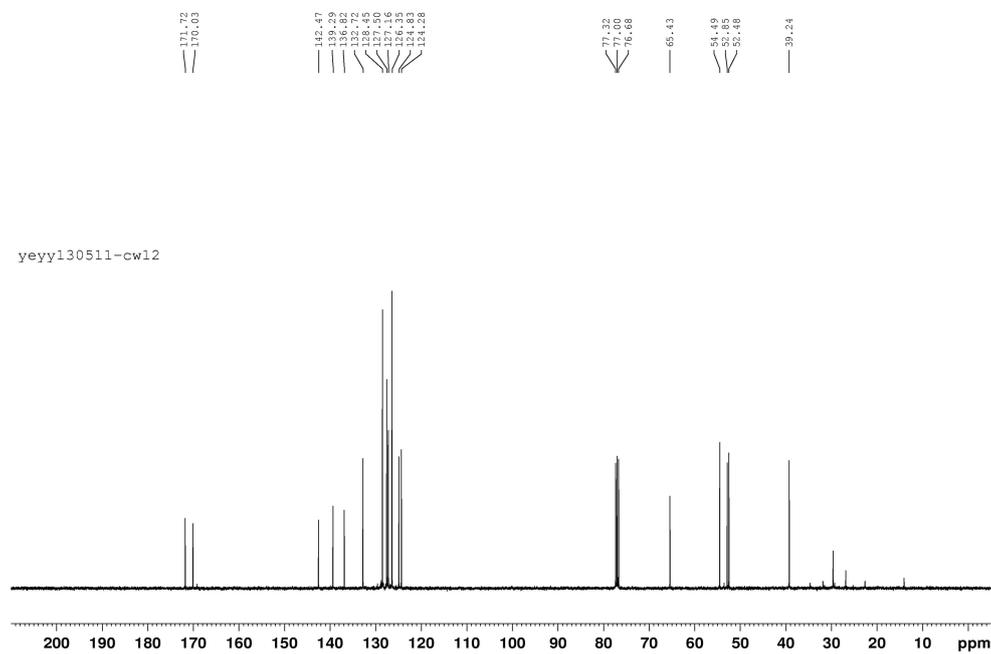
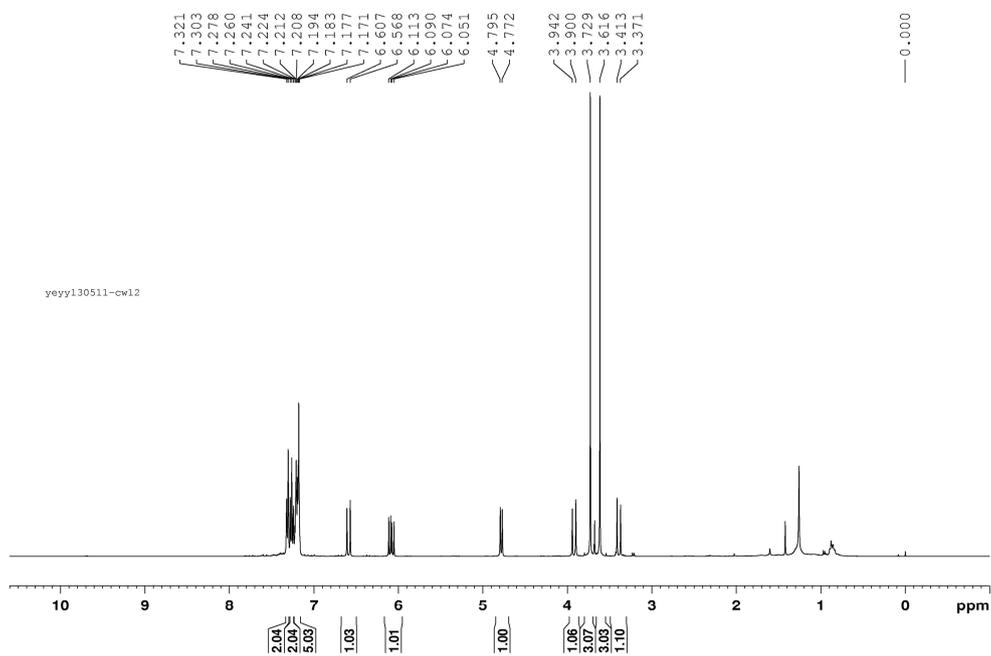
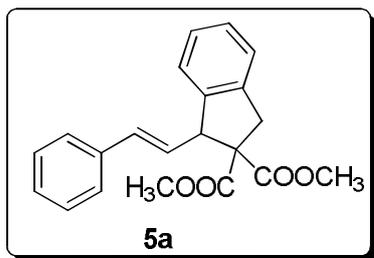


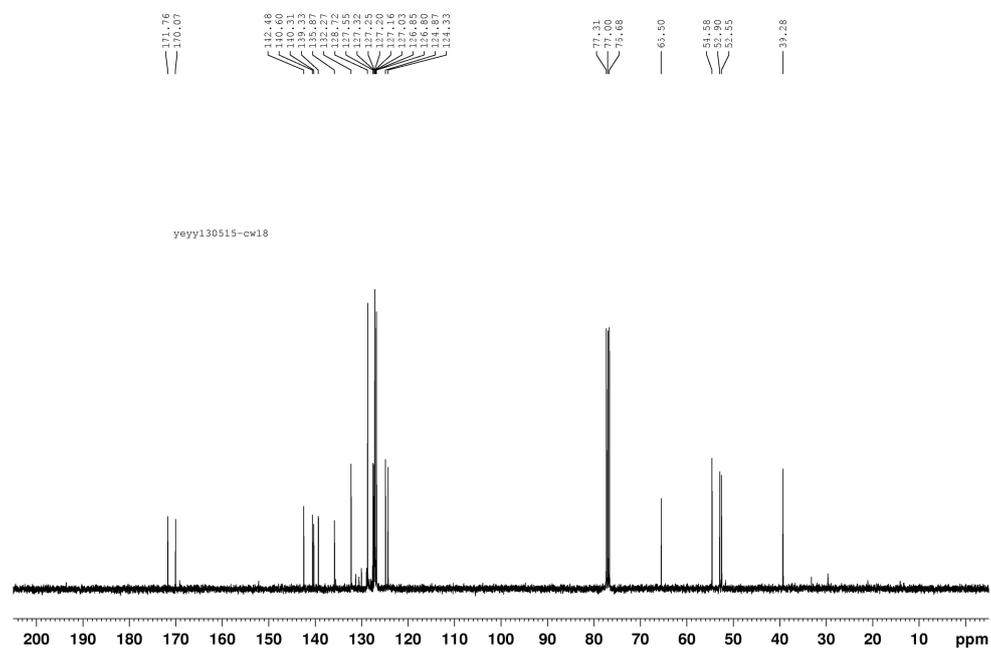
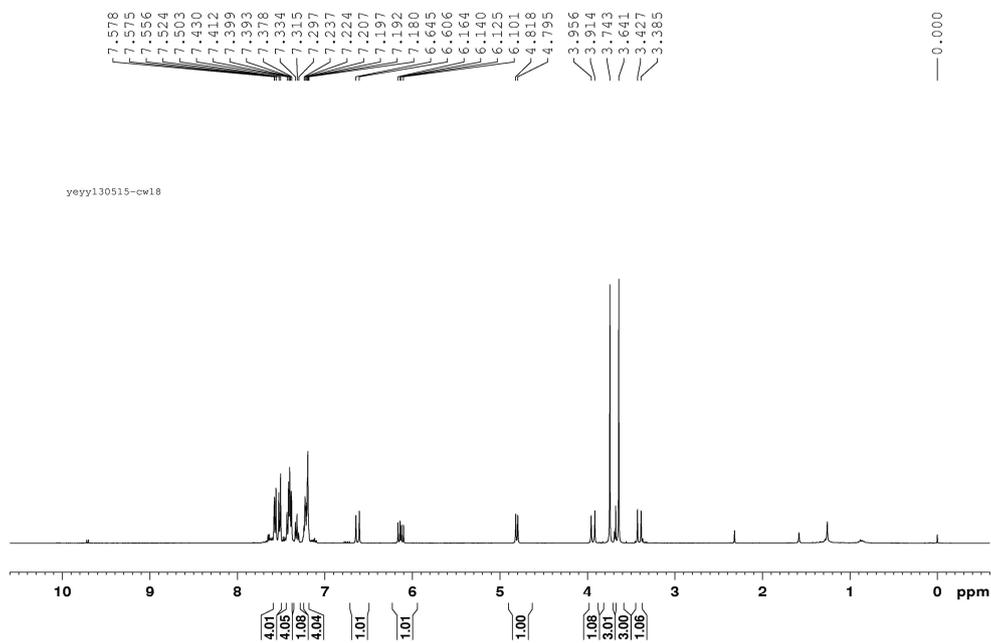
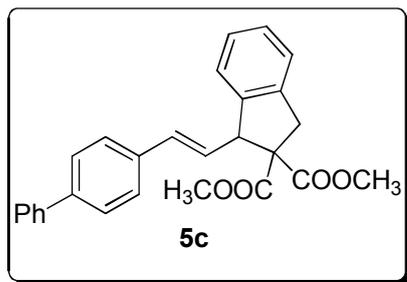


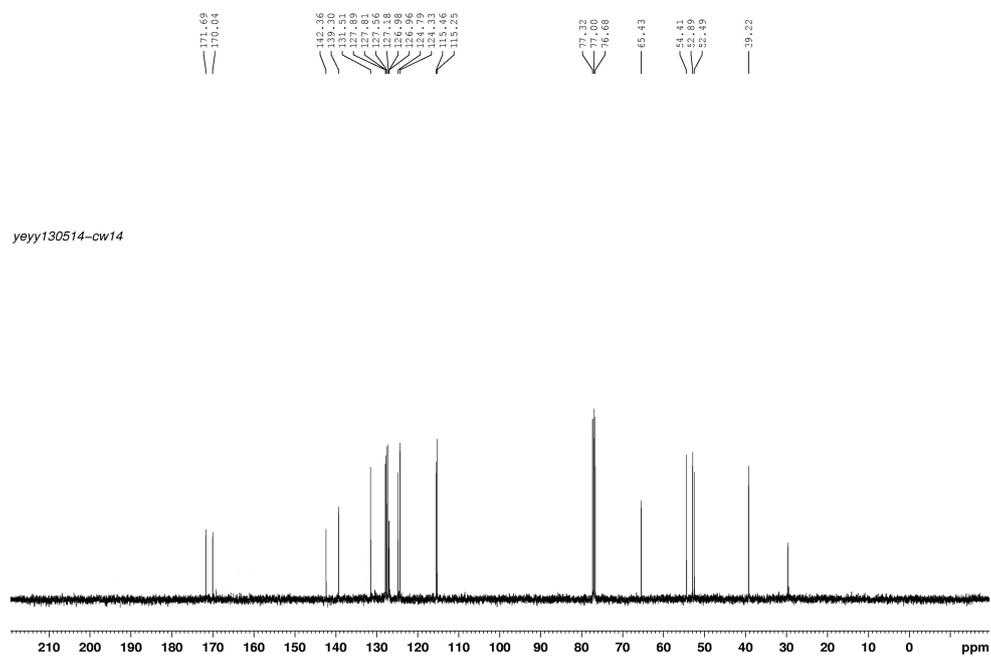
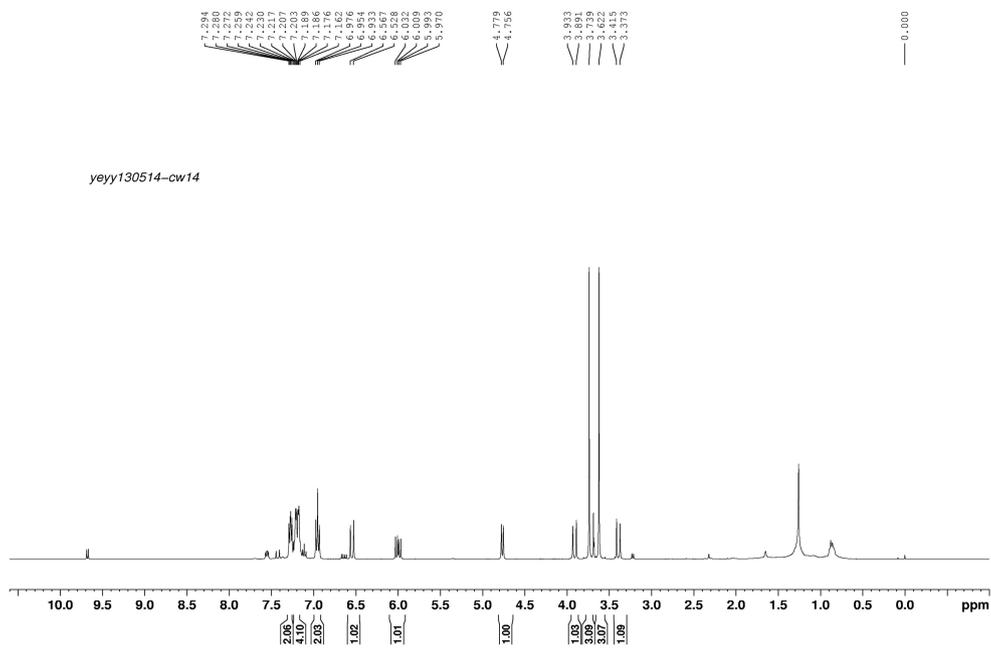
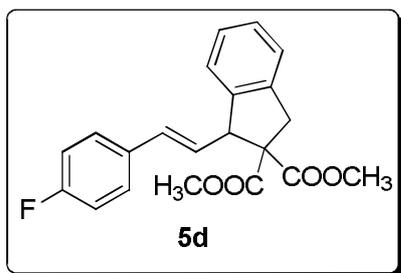


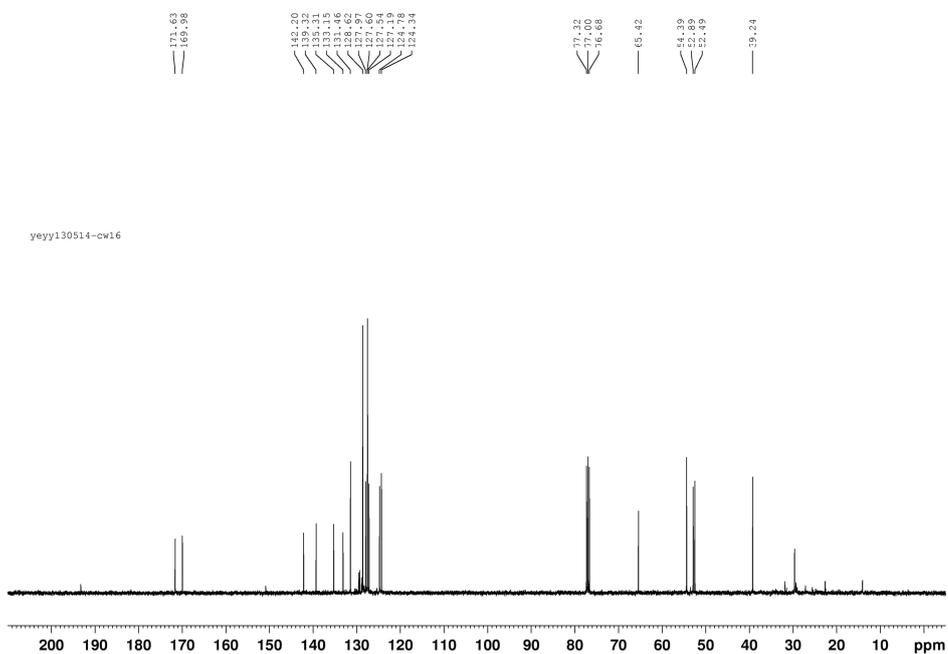
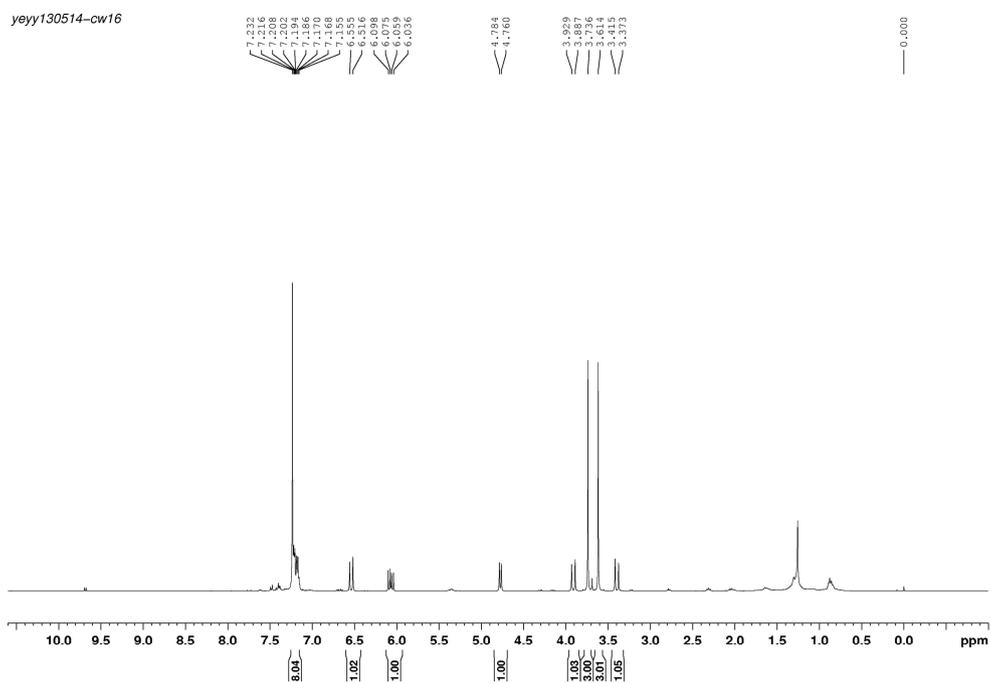
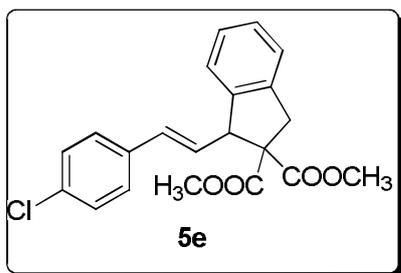


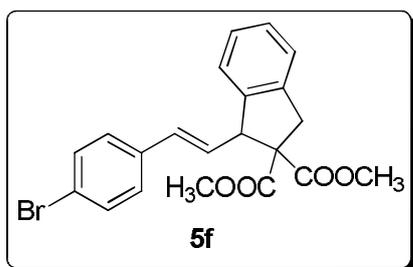




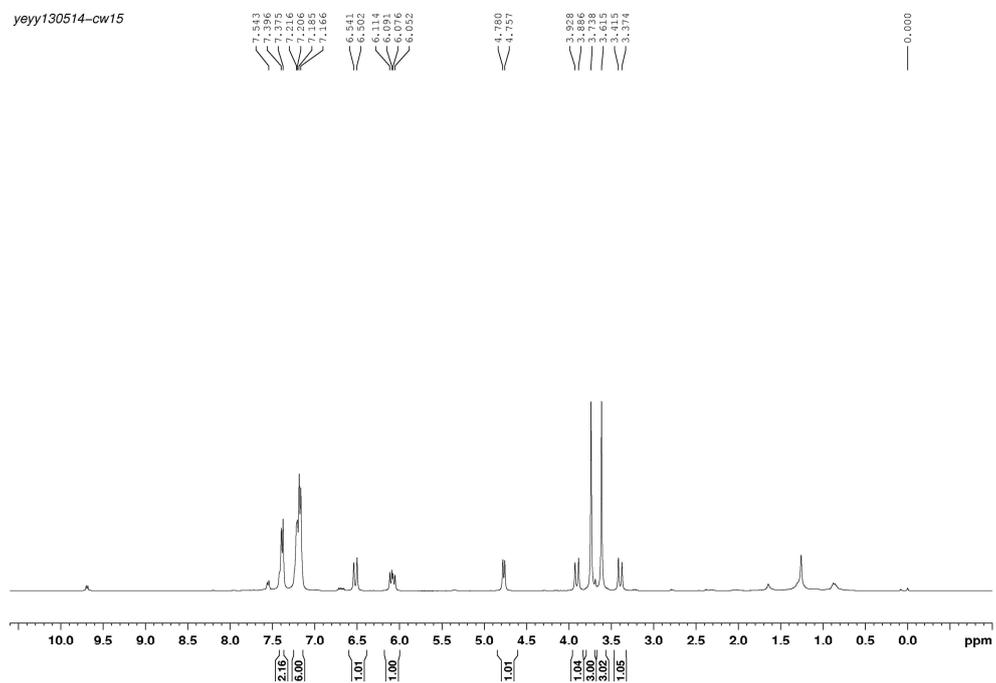








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yeyy130514--cw15

